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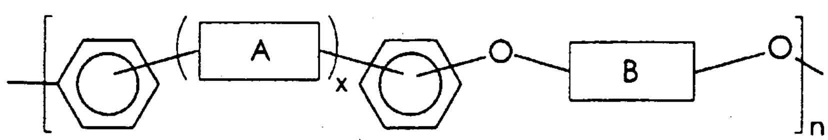
(54) **Blends containing curable polymers**

(57) Disclosed is a composition which comprises a mixture of (A) a first component comprising a polymer, at least some of the monomer repeat units of which have at least one photosensitivity-imparting group thereon, said polymer having a first degree of photosensitivity-imparting group substitution and being of the general formula



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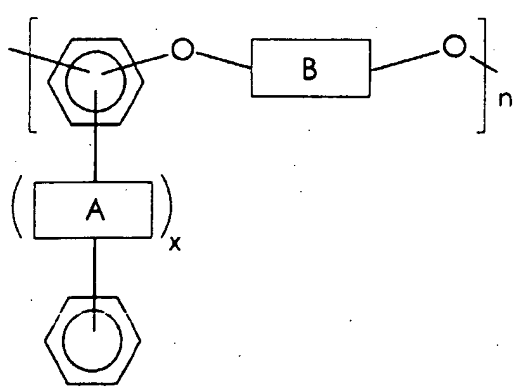

wherein x is an integer of 0 or 1, A and B are specified groups, and n is an integer representing the number of repeating monomer units, and (B) a second component which comprises either (1) a polymer having a second degree of photosensitivity-imparting group substitution or (2) a reactive diluent having at least one photosensitivity-imparting group.

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per molecule and having a fourth degree of photosensitivity-imparting group substitution. Also disclosed is a process for preparing a thermal ink jet printhead with the aforementioned composition.

Description

The present invention is directed to improved curable compositions. More specifically, the present invention is directed to compositions and processes which enable the preparation of compositions containing curable polymers, said compositions having uniform weight average molecular weight and a uniform degree of substitution with curable groups.

In microelectronics applications, there is a great need for low dielectric constant, high glass transition temperature, thermally stable, photopatternable polymers for use as interlayer dielectric layers and as passivation layers which protect microelectronic circuitry. Poly(imides) are widely used to satisfy these needs; these materials, however, have disadvantageous characteristics such as relatively high water sorption and hydrolytic instability. There is thus a need for high performance polymers which can be effectively photopatterned and developed at high resolution.

One particular application for such materials is the fabrication of ink jet printheads.

Other microelectronics applications include printed circuit boards, lithographic printing processes, and interlayer dielectrics.

Copending application U.S. Serial No. 08/705,375 discloses an improved composition comprising a defined photopatternable polymer containing at least some monomer repeat units with photosensitivity-imparting substituents.

Copending application U.S. Serial No. 08/705,365 discloses a composition which comprises (a) a defined polymer containing at least some monomer repeat units with photosensitivity-imparting substituents which enable crosslinking or chain extension of the polymer upon exposure to actinic radiation, wherein said photosensitivity-imparting substituents are hydroxyalkyl groups; (b) at least one member selected from the group consisting of photoinitiators and sensitizers; and (c) an optional solvent.

Copending application U.S. Serial No. 08/705,488 discloses a composition comprising a polymer with a weight average molecular weight of from about 1,000 to about 65,000, said polymer containing at least some monomer repeat units with a first, photosensitivity-imparting substituent which enables crosslinking or chain extension of the polymer upon exposure to actinic radiation, said polymer also containing a second, thermal sensitivity-imparting substituent which enables further polymerization of the polymer upon exposure to temperatures of about 140°C and higher.

Copending application U.S. Serial No. 08/697,761 discloses a process which comprises reacting a defined polymer with (i) a formaldehyde source, and (ii) an unsaturated acid in the presence of an acid catalyst, thereby forming a curable polymer with unsaturated ester groups.

Copending application U.S. Serial No. 08/705,463 discloses a process which comprises reacting a defined polymer with an acetyl halide and dimethoxymethane in the presence of a halogen-containing Lewis acid catalyst and methanol, thereby forming a haloalkylated polymer. In a specific embodiment, the haloalkylated polymer is then reacted further to replace at least some of the haloalkyl groups with photosensitivity-imparting groups.

Copending application U.S. Serial No. 08/705,479 discloses a process which comprises reacting a haloalkylated aromatic polymer with a material selected from the group consisting of unsaturated ester salts, alkoxide salts, alkylcarboxylate salts, and mixtures thereof, thereby forming a curable polymer having functional groups corresponding to the selected salt.

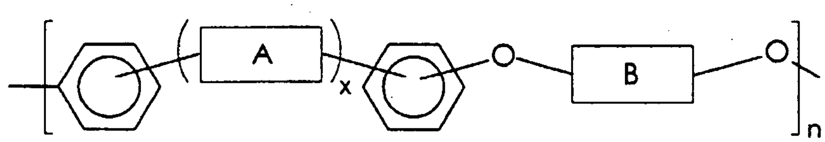
Copending application U.S. Serial No. 08/705,372 discloses a composition which comprises a defined polymer containing at least some monomer repeat units with photosensitivity-imparting substituents which enable crosslinking or chain extension of the polymer upon exposure to actinic radiation wherein said photosensitivity-imparting substituents are allyl ether groups, epoxy groups, or mixtures thereof.

Copending application U.S. Serial No. 08/697,760 discloses a composition which comprises a defined polymer containing at least some monomer repeat units with water-solubility-imparting substituents and at least some monomer repeat units with photosensitivity-imparting substituents which enable crosslinking or chain extension of the polymer upon exposure to actinic radiation.

While known compositions and processes are suitable for their intended purposes, a need remains for improved materials suitable for microelectronics applications. A need also remains for improved ink jet printheads. Further, there is a need for photopatternable polymeric materials which are heat stable, electrically insulating, and mechanically robust. Additionally, there is a need for photopatternable polymeric materials which are chemically inert with respect to the materials that might be employed in ink jet ink compositions. There is also a need for photopatternable polymeric materials which exhibit low shrinkage during post-cure steps in microelectronic device fabrication processes. In addition, a need remains for photopatternable polymeric materials which exhibit a relatively long shelf life. Further, there is a need for photopatternable polymeric materials which can be patterned with relatively low photo-exposure energies. Additionally, a need remains for photopatternable polymeric materials which, in the cured form, exhibit good solvent resistance. There is also a need for photopatternable polymeric materials which, when applied to microelectronic devices by spin casting techniques and cured, exhibit reduced edge bead and no apparent lips and dips. In addition, there remains a need for processes for preparing photopatternable polymeric materials with the above advantages. Further, a need remains for methods of maintaining consistent and uniform imaging qualities when preparing batches

of photopatternable polymeric materials. Additionally, there is a need for methods of controlling the degree of photosensitivity-imparting group substitution in a photoresist composition containing photosensitivity-imparting group substituted photopatternable polymers. Further, a need remains for photopatternable polymeric materials which exhibit no flow and no loss in patterned features subsequent to imaging, development, and thermal aging. In addition, there remains a need for photopatternable polymeric materials which have relatively low dielectric constants. Further, there is a need for photopatternable polymeric materials which exhibit reduced water sorption. Additionally, a need remains for photopatternable polymeric materials which exhibit improved hydrolytic stability, especially upon exposure to alkaline solutions. A need also remains for photopatternable polymeric materials which are stable at high temperatures, typically greater than about 150°C. There is also a need for photopatternable polymeric materials which either have high glass transition temperatures or are sufficiently crosslinked that there are no low temperature phase transitions subsequent to photoexposure. Further, a need remains for photopatternable polymeric materials with low coefficients of thermal expansion. In addition, there is a need for methods of preparing photoresist compositions with consistent processing conditions from different base resins. A need further remains for photoresist compositions with good to excellent reproducible processing characteristics. There is a need for polymers which are thermally stable, patternable as thick films of about 30 microns or more, exhibit low T_g prior to photoexposure, have low dielectric constants, are low in water absorption, have low coefficients of expansion, have desirable mechanical and adhesive characteristics, and are generally desirable for interlayer dielectric applications, including those at high temperatures, which are also photopatternable. There is also a need for photoresist compositions with good to excellent processing characteristics.

According to one aspect of the present invention, there is provided a composition which comprises a mixture of (A) a first component comprising a polymer, at least some of the monomer repeat units of which have at least one photosensitivity-imparting group thereon, said polymer having a first degree of photosensitivity-imparting group substitution measured in milliequivalents of photosensitivity-imparting group per gram and being of the general formula



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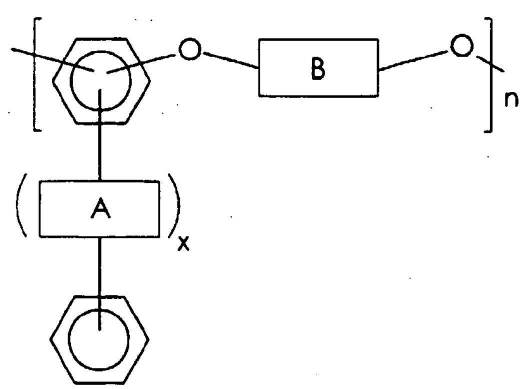
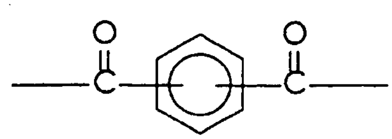
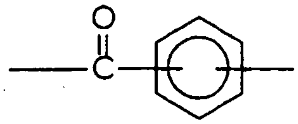
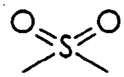
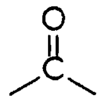


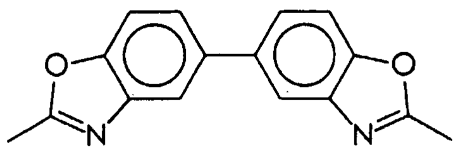
wherein x is an integer of 0 or 1, A is

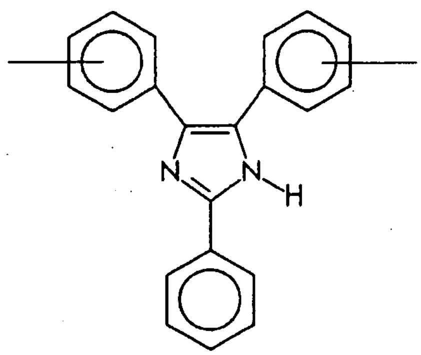


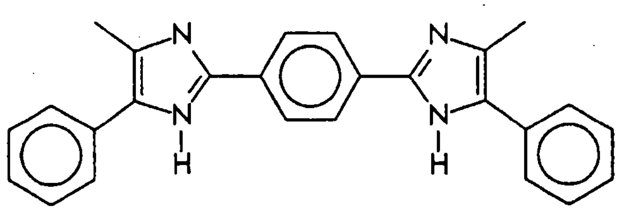


,

,

,

,

.

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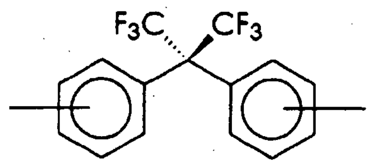
$-C(CH_3)_2-$,

or mixtures thereof, B is



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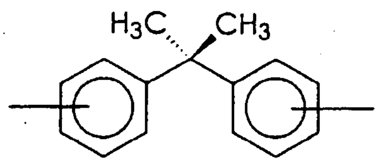

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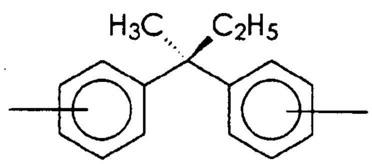

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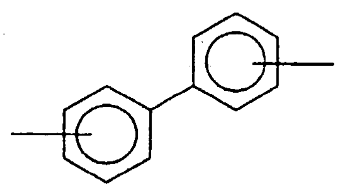

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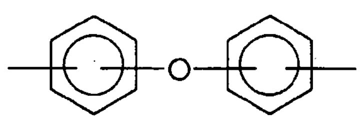

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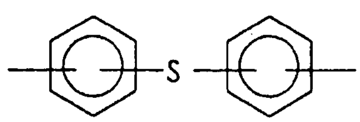

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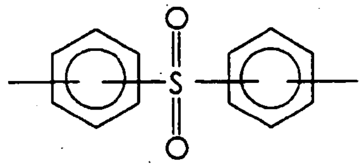

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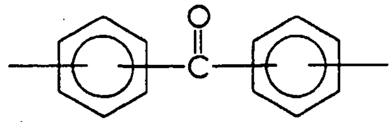

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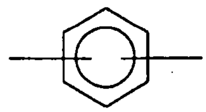

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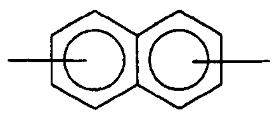

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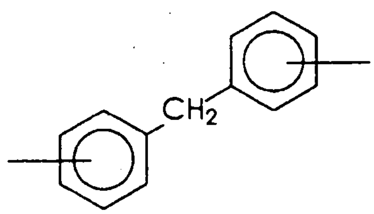

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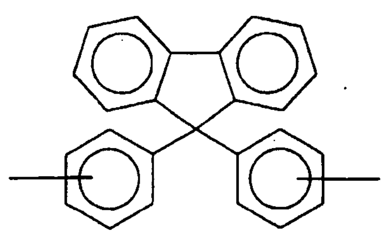

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$$-(CH_2)_v-$$

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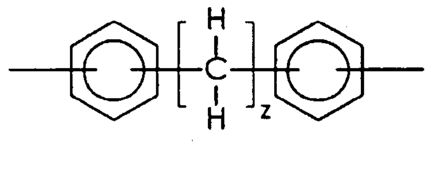
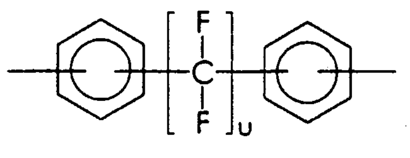
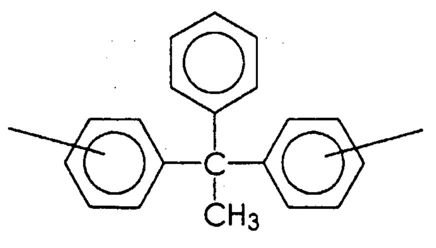
wherein v is an integer of from 1 to about 20,

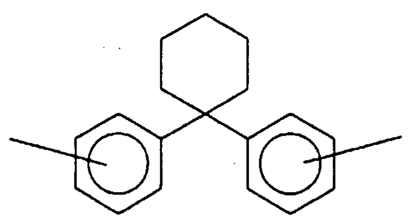


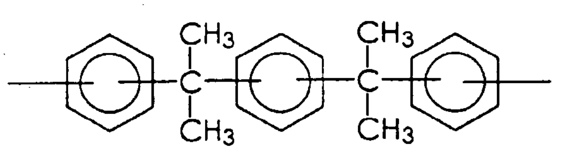
wherein z is an integer of from 2 to about 20,

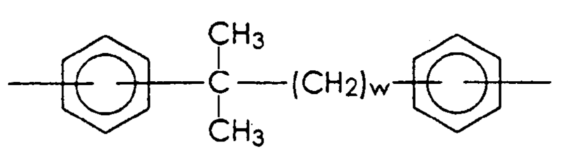


wherein u is an integer of from 1 to about 20,

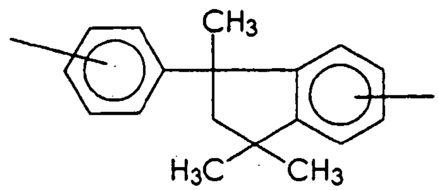


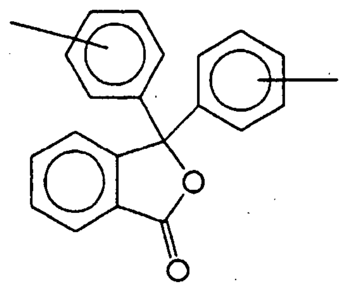


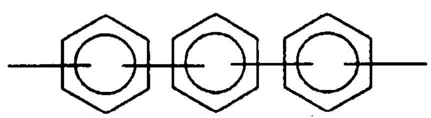


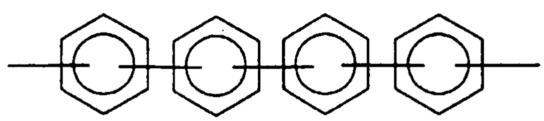


wherein w is an integer of from 1 to about 20,





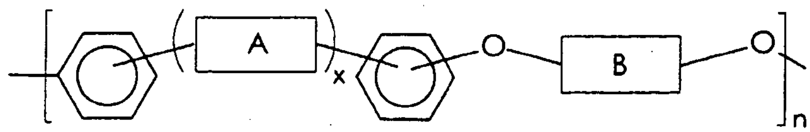




or mixtures thereof, and n is an integer representing the number of repeating monomer units, and (B) a second component which comprises either (1) a polymer having a second degree of photosensitivity-imparting group substitution measured in milliequivalents of photosensitivity-imparting group per gram lower than the first degree of photosensitivity-imparting group substitution, wherein said second degree of photosensitivity-imparting group substitution may be zero, wherein the mixture of the first component and the second component has a third degree of photosensitivity-imparting group substitution measured in milliequivalents of photosensitivity-imparting group per gram which is lower than the first degree of photosensitivity-imparting group substitution and higher than the second degree of photosensitivity-imparting group substitution, or (2) a reactive diluent having at least one photosensitivity-imparting group per molecule and having a fourth degree of photosensitivity-imparting group substitution measured in milliequivalents of photosensitivity-imparting group per gram, wherein the mixture of the first component and the second component has a fifth degree of photosensitivity-imparting group substitution measured in milliequivalents of photosensitivity-imparting group per gram which is higher than the first degree of photosensitivity-imparting group substitution and lower than the fourth degree of photosensitivity-imparting group substitution; wherein the weight average molecular weight of the mixture is from about 10,000 to about 50,000; and wherein the third or fifth degree of photosensitivity-imparting group substitution is from about 0.25 to about 2 milliequivalents of photosensitivity-imparting groups per gram of mixture.

According to a process of the present invention, there is provided a process for preparing a photocurable composition having uniform weight average molecular weight and a uniform degree of unsaturated ester substitution, said process comprising the steps of: (a) providing a first component comprising a polymer, at least some of the monomer repeat units of which have at least one photosensitivity-imparting group thereon, said polymer having a first degree of

photosensitivity-imparting group substitution measured in milliequivalents of photosensitivity-imparting group per gram and being of the formula



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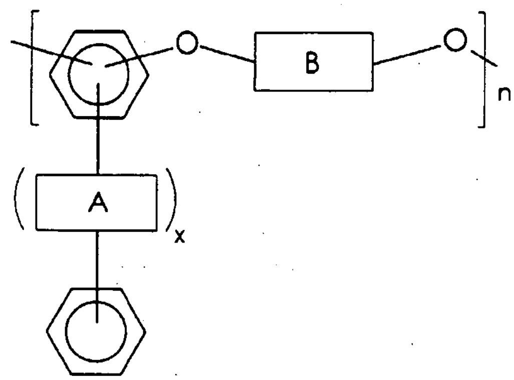

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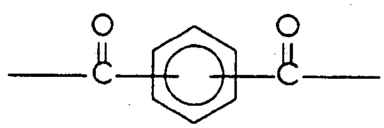

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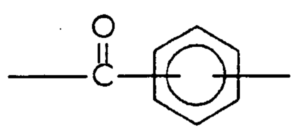

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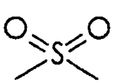

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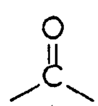

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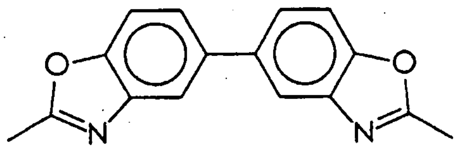

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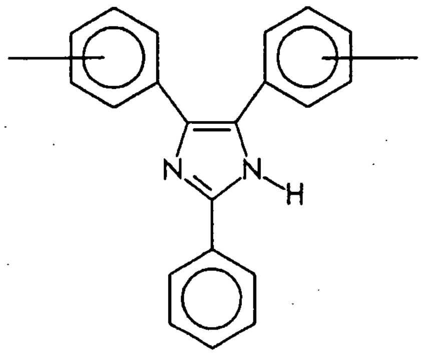

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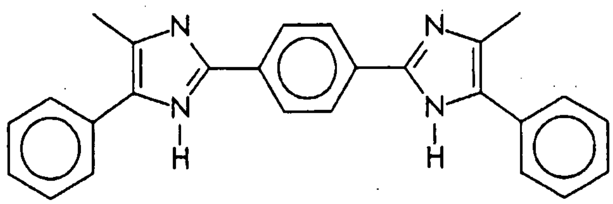

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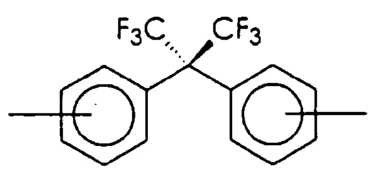

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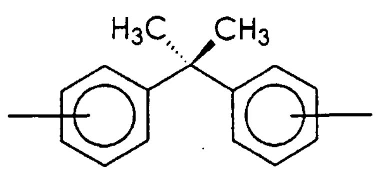

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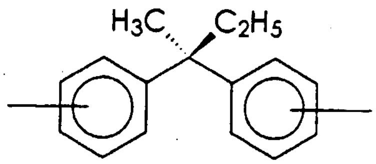

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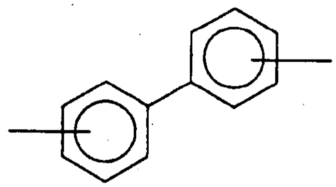

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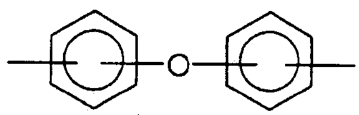

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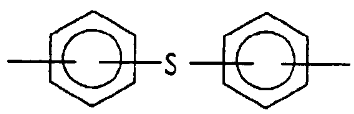

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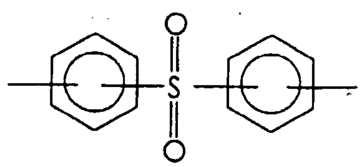

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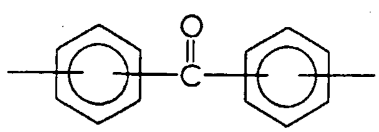

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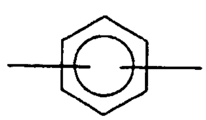

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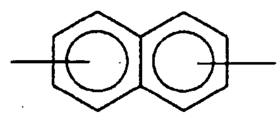

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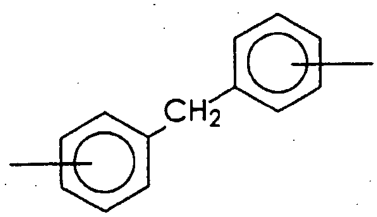

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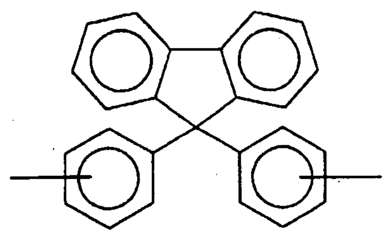

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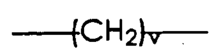
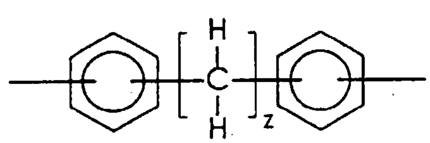


,

wherein v is an integer of from 1 to about 20,



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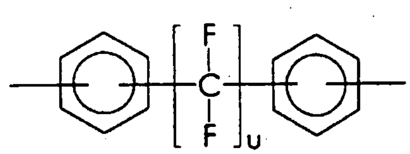
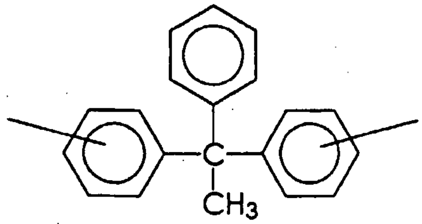
wherein z is an integer of from 2 to about 20,



,

wherein u is an integer of from 1 to about 20,



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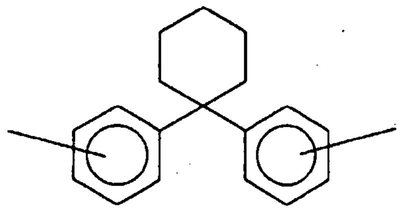

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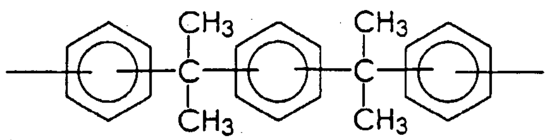

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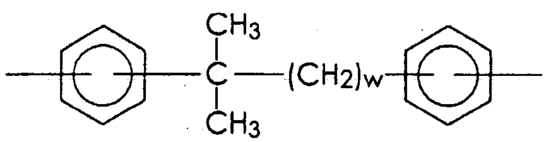

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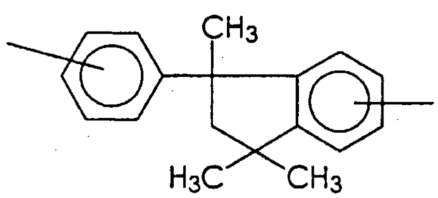
wherein w is an integer of from 1 to about 20,



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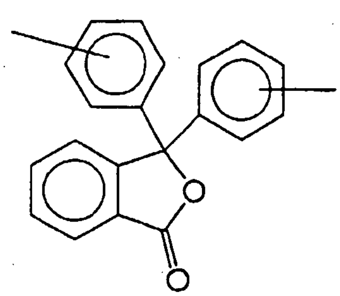

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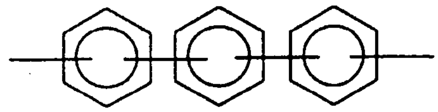

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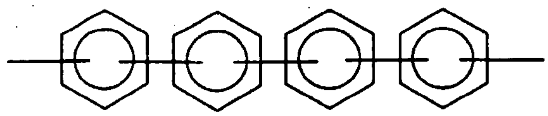


,

or mixtures thereof, and n is an integer representing the number of repeating monomer units; (b) providing a second component which comprises either (1) a polymer having a second degree of photosensitivity-imparting group substitution measured in milliequivalents of photosensitivity-imparting group per gram lower than the first degree of photosensitivity-imparting group substitution, wherein said second degree of photosensitivity-imparting group substitution may be zero, or (2) a reactive diluent having at least one photosensitivity-imparting group per molecule and having a fourth degree of photosensitivity-imparting group substitution measured in milliequivalents of photosensitivity-imparting group per gram; and (c) admixing the first component and the second component in relative amounts to result in either (1) a mixture of the first component and the polymer having a second degree of photosensitivity-imparting group substitution, said mixture having a third degree of photosensitivity-imparting group substitution which is lower than the first degree of photosensitivity-imparting group substitution and higher than the second degree of photosensitivity-imparting group substitution, or (2) a mixture of the first component and the reactive diluent having at least one photosensitivity-imparting group per molecule and having a fourth degree of photosensitivity-imparting group substitution, said mixture having a fifth degree of photosensitivity-imparting group substitution measured in milliequivalents of photosensitivity-imparting group per gram which is higher than the first degree of photosensitivity-imparting group substitution and lower than the fourth degree of photosensitivity-imparting group substitution; said mixture having a weight average molecular weight of from about 10,000 to about 50,000, wherein the third or fifth degree of photosensitivity-imparting group substitution is from about 0.25 to about 2 milliequivalents of photosensitivity-imparting groups per gram of mixture.

According to another aspect of the present invention, there is provided a process for making an ink jet printhead comprising the steps of: (a) depositing a layer comprising a polymer-containing composition onto a lower substrate in which one surface thereof has an array of heating elements and addressing electrodes having terminal ends formed thereon, said polymer being deposited onto the surface having the heating elements and addressing electrodes thereon; (b) exposing the layer to actinic radiation in an imagewise pattern such that the polymer in exposed areas becomes crosslinked or chain extended and the polymer in unexposed areas does not become crosslinked or chain extended, wherein the unexposed areas correspond to areas of the lower substrate having thereon the heating elements and the terminal ends of the addressing electrodes; (c) removing the polymer from the unexposed areas, thereby forming recesses in the layer, said recesses exposing the heating elements and the terminal ends of the addressing electrodes; (d) providing an upper substrate with a set of parallel grooves for subsequent use as ink channels and a recess for subsequent use as a manifold, the grooves being open at one end for serving as droplet emitting nozzles; and (e) aligning, mating, and bonding the upper and lower substrates together to form a printhead with the grooves in the upper substrate being aligned with the heating elements in the lower substrate to form droplet emitting nozzles, thereby forming an ink jet printhead.

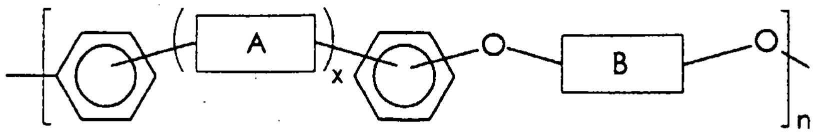
Figure 1 is an enlarged schematic isometric view of an example of a printhead mounted on a daughter board showing the droplet emitting nozzles.

Figure 2 is an enlarged cross-sectional view of Figure 1 as viewed along the line 2-2 thereof and showing the electrode passivation and ink flow path between the manifold and the ink channels.

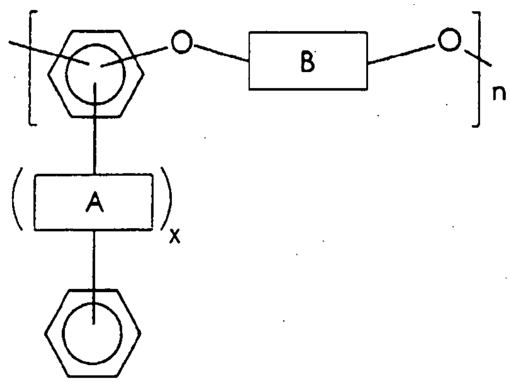
Figure 3 is an enlarged cross-sectional view of an alternate embodiment of the printhead in Figure 1 as viewed along the line 2-2 thereof.

The present invention is directed to compositions and processes which enable the preparation of photosensitivity-imparting-group substituted polymer blends which have uniform weight average molecular weight and a uniform degree of substitution.

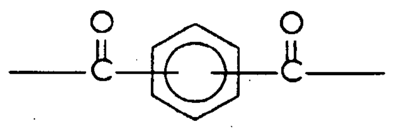
The polymers of the present invention are prepared from polymers of the following formula:

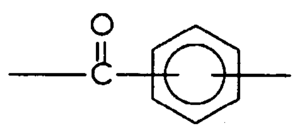


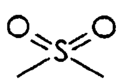
or

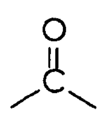


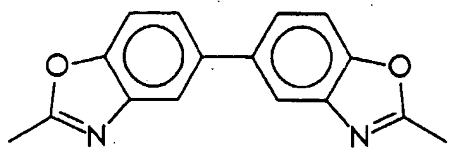
wherein x is an integer of 0 or 1, A is











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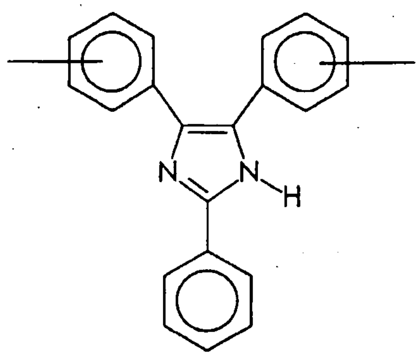

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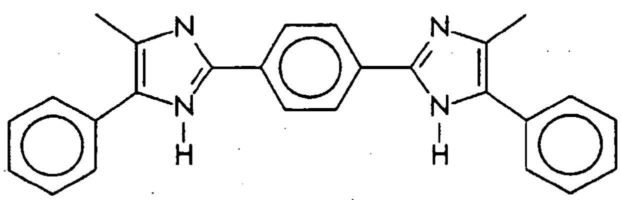
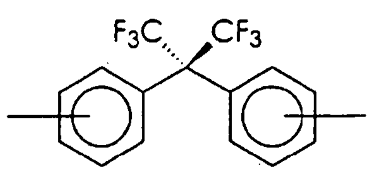


,

-O-,

$-C(CH_3)_2-$,

or mixtures thereof, B is



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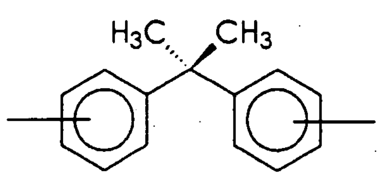

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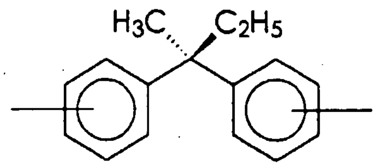

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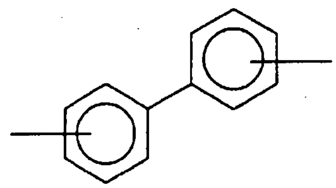

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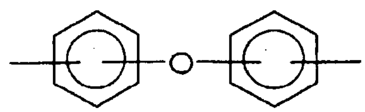

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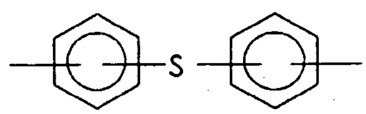

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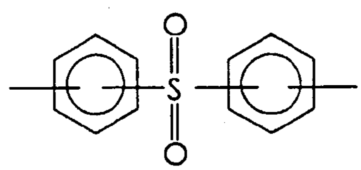

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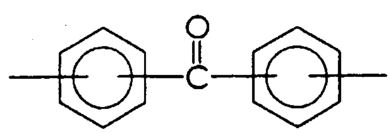

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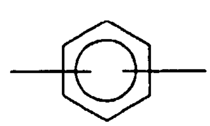

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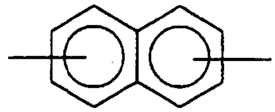

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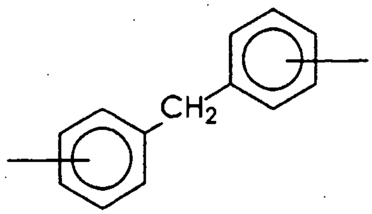

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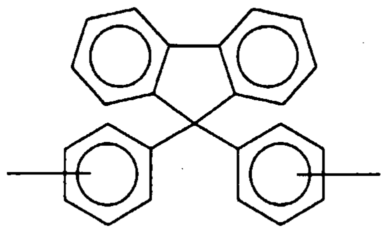

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$$-(CH_2)_v-$$

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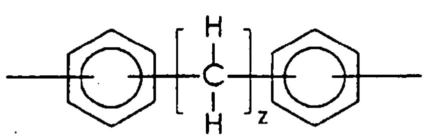
wherein v is an integer of from 1 to about 20, and preferably from 1 to about 10,



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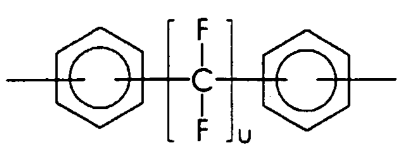
wherein z is an integer of from 2 to about 20, and preferably from 2 to about 10,



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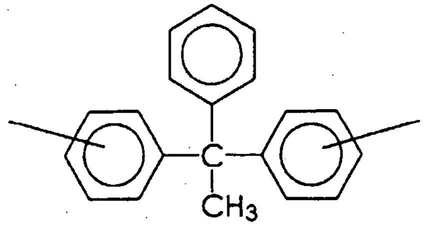
wherein u is an integer of from 1 to about 20, and preferably from 1 to about 10,



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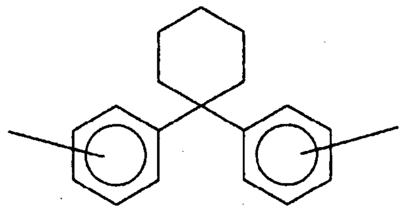

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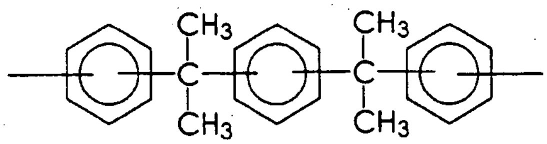

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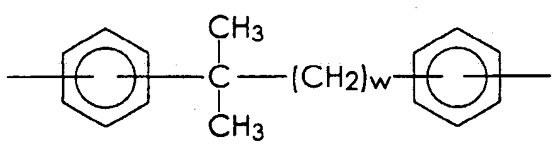

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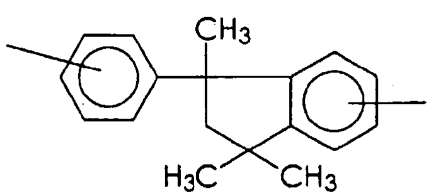
wherein w is an integer of from 1 to about 20, and preferably from 1 to about 10,



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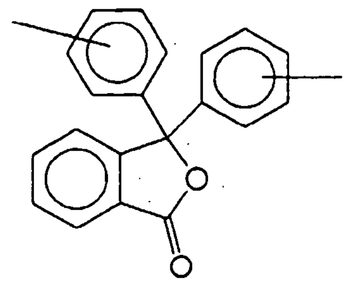
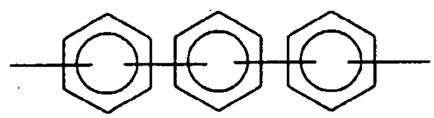
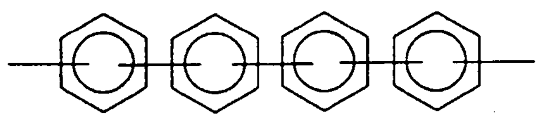






other similar bisphenol derivatives, or mixtures thereof, and n is an integer representing the number of repeating monomer units. The value of n is such that the weight average molecular weight of the material typically is from about 1,000 to about 100,000, preferably from about 1,000 to about 65,000, more preferably from about 1,000 to about 40,000, and even more preferably from about 3,000 to about 25,000, although the weight average molecular weight can be outside these ranges. Preferably, n is an integer of from about 2 to about 70, more preferably from about 5 to about 70, and even more preferably from about 8 to about 50, although the value of n can be outside these ranges. The phenyl groups and the A and/or B groups may also be substituted, although the presence of two or more substituents on the B group ortho to the oxygen groups can render substitution difficult. Substituents can be present on the polymer either prior to or subsequent to the placement of photosensitivity-imparting functional groups thereon. Substituents can also be placed on the polymer during the process of placement of photosensitivity-imparting functional groups thereon. Examples of suitable substituents include (but are not limited to) alkyl groups, including saturated, unsaturated, and cyclic alkyl groups, preferably with from 1 to about 6 carbon atoms, substituted alkyl groups, including saturated, unsaturated, and cyclic substituted alkyl groups, preferably with from 1 to about 6 carbon atoms, aryl groups, preferably with from 6 to about 24 carbon atoms, substituted aryl groups, preferably with from 6 to about 24 carbon atoms, arylalkyl groups, preferably with from 7 to about 30 carbon atoms, substituted arylalkyl groups, preferably with from 7 to about 30 carbon atoms, alkoxy groups, preferably with from 1 to about 6 carbon atoms, substituted alkoxy groups, preferably with from 1 to about 6 carbon atoms, aryloxy groups, preferably with from 6 to about 24 carbon atoms, substituted aryloxy groups, preferably with from 6 to about 24 carbon atoms, arylalkyloxy groups, preferably with from 7 to about 30 carbon atoms, substituted arylalkyloxy groups, preferably with from 7 to about 30 carbon atoms, hydroxy groups, amine groups, imine groups, ammonium groups, pyridine groups, pyridinium groups, ether groups, ester groups, amide groups, carbonyl groups, thiocarbonyl groups, sulfate groups, sulfonate groups, sulfide groups, sulfoxide groups, phosphine groups, phosphonium groups, phosphate groups, mercapto groups, nitroso groups, sulfone groups, acyl groups, acid anhydride groups, azide groups, and the like, wherein the substituents on the substituted alkyl groups, substituted aryl groups, substituted arylalkyl groups, substituted alkoxy groups, substituted aryloxy groups, and substituted arylalkyloxy groups can be (but are not limited to) hydroxy groups, amine groups, imine groups, ammonium groups, pyridine groups, pyridinium groups, ether groups, aldehyde groups, ketone groups, ester groups, amide groups, carboxylic acid groups, carbonyl groups, thiocarbonyl groups, sulfate groups, sulfonate groups, sulfide groups, sulfoxide groups, phosphine groups, phosphonium groups, phosphate groups, cyano groups, nitrile groups, mercapto groups, nitroso groups, halogen atoms, nitro groups, sulfone groups, acyl groups, acid anhydride groups, azide groups, mixtures thereof, and

the like, wherein two or more substituents can be joined together to form a ring. Processes for the preparation of these materials are known, and disclosed in, for example, P. M. Hergenrother, *J. Macromol. Sci. Rev. Macromol. Chem.*, ***C19*** (1), 1-34 (1980); P. M. Hergenrother, B. J. Jensen, and S. J. Havens, *Polymer*, ***29***, 358 (1988); B. J. Jensen and P.M. Hergenrother, "High Performance Polymers," Vol. 1, No. 1) page 31 (1989), "Effect of Molecular Weight on Poly(arylene ether ketone) Properties"; V. Percec and B. C. Auman, *Makromol. Chem.* ***185***, 2319 (1984); "High Molecular Weight Polymers by Nickel Coupling of Aryl Polychlorides," I. Colon, G. T. Kwaiatkowski, J. *of Polymer Science, Part A, Polymer Chemistry*, ***28***, 367 (1990); M. Ueda and T. Ito, *Polymer J.*, ***23*** (4), 297 (1991); "Ethynyl-Terminated Polyarylates: Synthesis and Characterization," S. J. Havens and P. M. Hergenrother, J. *of Polymer Science: Polymer Chemistry Edition*, ***22***, 3011 (1984); "Ethynyl-Terminated Polysulfones: Synthesis and Characterization," P. M. Hergenrother, *J. of Polymer Science: Polymer Chemistry Edition*, ***20***, 3131 (1982); K. E. Dukes, M. D. Forbes, A. S. Jeevarajan, A. M. Belu, J. M. DeDimone, R. W. Linton, and V. V. Sheares, *Macromolecules*, ***29***, 3081 (1996); G. Hougham, G. Tesoro, and J. Shaw, *Polym. Mater Sci. Eng.*, ***61***, 369 (1989); V. Percec and B. C. Auman, *Makromol. Chem*, ***185***, 617 (1984); "Synthesis and characterization of New Fluorescent Poly(arylene ethers)," S. Matsuo, N. Yakoh, S. Chino, M. Mitani, and S. Tagami, *Journal of Polymer Science: Part A: Polymer Chemistry*, ***32***, 1071 (1994); "Synthesis of a Novel Naphthalene-Based Poly(arylene ether ketone) with High Solubility and Thermal Stability," Mami Ohno, Toshikazu Takata, and Takeshi Endo, *Macromolecules*, ***27***, 3447 (1994); "Synthesis and Characterization of New Aromatic Poly(ether ketones)," F. W. Mercer, M. T. Mckenzie, G. Merlino, and M. M. Fone, *J. of Applied Polymer Science*, ***56***, 1397 (1995); H. C. Zhang, T. L. Chen, Y. G. Yuan, Chinese Patent CN 85108751 (1991); "Static and laser light scattering study of novel thermoplastics. 1. Phenolphthalein poly(aryl ether ketone)," C. Wu, S. Bo, M. Siddiq, G. Yang and T. Chen, *Macromolecules*, ***29***, 2989 (1996); "Synthesis of t-Butyl-Substituted Poly(ether ketone) by Nickel-Catalyzed Coupling Polymerization of Aromatic Dichloride", M. Ueda, Y. Seino, Y. Haneda, M. Yoneda, and J.-I. Sugiyama, *Journal of Polymer Science: Part A: Polymer Chemistry*, ***32***, 675 (1994); "Reaction Mechanisms: Comb-Like Polymers and Graft Copolymers from Macromers 2. Synthesis, Characterzation and Homopolymerization of a Styrene Macromer of Poly(2,6-dimethyl-1,4-phenylene Oxide)," V. Percec, P. L. Rinaldi, and B. C. Auman, *Polymer Bulletin*, ***10***, 397 (1983); *Handbook of Polymer Synthesis Part A*, Hans R. Kricheldorf, ed., Marcel Dekker, Inc., New York-Basel-Hong Kong (1992); and "Introduction of Carboxyl Groups into Crosslinked Polystyrene," C. R. Harrison, P. Hodge, J. Kemp, and G. M. Perry, *Die Makromolekulare Chemie*, ***176***, 267 (1975), the disclosures of each of which are totally incorporated herein by reference.

For applications wherein the photopatternable polymer is to be used as a layer in a thermal ink jet printhead, the polymer preferably has a number average molecular weight of from about 3,000 to about 20,000, more preferably from about 3,000 to about 10,000, and even more preferably from about 3,500 to about 6,500, although the molecular weight can be outside this range.

The photopatternable polymers of the present invention contain in at least some of the monomer repeat units thereof photosensitivity-imparting substituents which enable crosslinking or chain extension of the polymer upon exposure to actinic radiation. Radiation which activates crosslinking or chain extension can be of any desired source and any desired wavelength, including (but not limited to) visible light, infrared light, ultraviolet light, electron beam radiation, x-ray radiation, or the like. Examples of suitable photosensitivity imparting groups include unsaturated ester groups, such as acryloyl groups, methacryloyl groups, cinnamoyl groups, crotonoyl groups, ethacryloyl groups, oleoyl groups, linoleoyl groups, maleoyl groups, fumaroyl groups, itaconoyl groups, citraconoyl groups, phenylmaleoyl groups, esters of 3-hexene-1,6-dicarboxylic acid, and the like. Also suitable are alkylcarboxymethylene and ether groups. Under certain conditions, such as imaging with electron beam, deep ultraviolet, or x-ray radiation, halomethyl groups are also photoactive. Epoxy groups, allyl ether groups, hydroxyalkyl groups, and unsaturated ammonium, unsaturated phosphonium, and unsaturated ether groups are also suitable photoactive groups.

The photopatternable polymers containing these groups can be prepared by any suitable or desired process. For example, the desired functional group or groups can be applied directly to the polymer. Alternatively, one or more intermediate materials can be prepared. For example, the polymer backbone can be functionalized with a substituent which allows for the facile derivatization of the polymer backbone, such as hydroxyl groups, carboxyl groups, haloalkyl groups such as chloromethyl groups, hydroxyalkyl groups such as hydroxy methyl groups, alkoxy methyl groups, alkylcarboxymethylene groups, and the like.

Unsaturated ester groups can be placed on the polymer backbone by any suitable or desired process, including that described in US Serial No. 08/697,761. For example, substitution of the polymer can be accomplished by reacting the polymer in solution with (a) the appropriate unsaturated acid (such as acrylic acid, methacrylic acid, cinnamic acid, crotonic acid, ethacrylic acid, oleic acid, linoleic acid, maleic acid, fumaric acid, itaconic acid, citraconic acid, phenylmaleic acid, 3-hexene-1,6-dicarboxylic acid, or the like), and (b) a formaldehyde source (i.e., either formaldehyde or a material which, under the conditions of the reaction, generates formaldehyde; examples of formaldehyde sources in addition to formaldehyde include paraformaldehyde, trioxane, methylal, dimethoxymethane, and the like). The reaction is direct acid catalyzed; the polymer is dissolved in a suitable solvent and is allowed to react with the formaldehyde source at about 105°C in the presence of catalytic amounts of para-toluenesulfonic acid. Examples of solvents suitable

for the reaction include 1,1,2,2-tetrachloroethane and, if a suitable pressure reactor is used, methylene chloride. Typically, the reactants are present in relative amounts with respect to each other (by weight) of about 10 parts polymer, about 5 parts formaldehyde source, about 1 part para-toluenesulfonic acid, about 15.8 parts of the appropriate acid (i. e., acrylic acid, methacrylic acid, or the like), about 0.2 parts hydroquinone methyl ether, and about 162 parts 1,1,2,2-tetrachloroethane.

Typical reaction temperatures are from about 25 to about 145°C, and preferably at about 105°C. Typical reaction times are from about 1 to about 6 hours, and preferably from about 2 to about 4 hours, although the time can be outside these ranges. Longer reaction times generally result in higher degrees of substitution. Higher degrees of substitution generally lead to greater photosensitivity of the polymer, and different degrees of substitution may be desirable for different applications. Too high a degree of substitution may lead to excessive sensitivity, resulting in crosslinking or chain extension of both exposed and unexposed polymer material when the material is exposed imagewise to activating radiation. Too low a degree of substitution may be undesirable because of resulting unnecessarily long exposure times or unnecessarily high exposure energies. For applications wherein the photopatternable polymer is to be used as a layer in a thermal ink jet printhead, the degree of substitution (i.e., the average number of unsaturated ester groups per monomer repeat unit) preferably is from about 0.25 to about 1.2, and more preferably from about 0.65 to about 0.8, although the degree of substitution can be outside these ranges for ink jet printhead applications. This degree of substitution generally corresponds to from about 0.5 to about 1.3 milliequivalents of unsaturated ester groups per gram of resin.

The polymers of the above general formula can also be substituted with photosensitivity-imparting groups such as unsaturated ester groups, ether groups, or alkylcarboxymethylene groups by first preparing the haloalkylated derivative and then replacing at least some of the haloalkyl groups with unsaturated ester, ether, or alkylcarboxymethylene groups. A suitable substitution reaction for this purpose is described in US Serial No. 08/705,479. For example, the haloalkylated polymer can be substituted with unsaturated ester, ether, or alkylcarboxymethylene groups by reacting the haloalkylated polymer with an unsaturated ester, alkoxide, or alkylcarboxylate salt in solution. Examples of suitable reactants include selected salts of Groups IA, IIB, IIIB, IVB, VB, VIB, VIIB, VIIIB, IB, IIB, IIIA, IVA, and the like, of the periodic table with the appropriate unsaturated ester, such as the ester salts of acrylic acid, methacrylic acid, cinnamic acid, crotonic acid, ethacrylic acid, oleic acid, linoleic acid, maleic acid, fumaric acid, itaconic acid, citraconic acid, phenylmaleic acid, 3-hexene-1,6-dicarboxylic acid, and the like, or the appropriate alkoxide or alkylcarboxylate, with specific examples including sodium, potassium, quaternary ammonium, phosphonium, and the like salts of acrylate, methacrylate, cinnamate, methoxide, acetate, and the like. Examples of solvents suitable for the reaction include polar aprotic solvents such as N,N-dimethylacetamide, dimethylsulfoxide, N-methylpyrrolidinone, dimethylformamide, and the like. Typically, the reactants are present in relative amounts with respect to each other by weight of about 10 parts haloalkylated polymer, about 66.5 parts solvent, and about 5.7 parts unsaturated ester salt.

Higher degrees of haloalkylation generally enable higher degrees of substitution with unsaturated ester, ether, and/or alkylcarboxymethylene groups and thereby enable greater photosensitivity of the polymer. Different degrees of substitution with unsaturated ester, ether, and/or alkylcarboxymethylene groups may be desirable for different applications. Too high a degree of substitution may lead to excessive sensitivity, resulting in crosslinking or chain extension of both exposed and unexposed polymer material when the material is exposed imagewise to activating radiation, whereas too low a degree of substitution may be undesirable because of resulting unnecessarily long exposure times or unnecessarily high exposure energies. For applications wherein the photopatternable polymer is to be used as a layer in a thermal ink jet printhead, the degree of substitution (i.e., the average number of unsaturated ester, ether, and/or alkylcarboxymethylene groups per monomer repeat unit) preferably is from about 0.5 to about 1.2, and more preferably from about 0.65 to about 0.8, although the degree of substitution can be outside these ranges for ink jet printhead applications. Optimum amounts of substitution with unsaturated ester, ether, and/or alkylcarboxymethylene groups are from about 0.8 to about 1.3 milliequivalents of unsaturated ester, ether, and/or alkylcarboxymethylene groups per gram of resin.

Some or all of the haloalkyl groups can be replaced with unsaturated ester, ether, and/or alkylcarboxymethylene substituents. Longer reaction times generally lead to greater degrees of substitution of haloalkyl groups with unsaturated ester, ether, and/or alkylcarboxymethylene substituents.

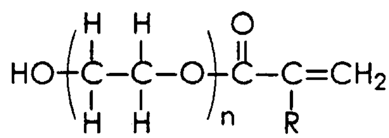
Typical reaction temperatures are from about 20 to about 35°C, and preferably about 25°C, although the temperature can be outside this range. Typical reaction times are from about 30 minutes to about 15 days, and preferably from about 2 hours to about 2 days, although the time can be outside these ranges.

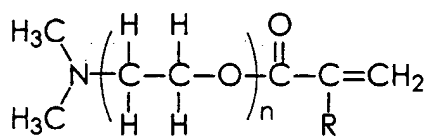
The haloalkylated polymer can be allyl ether substituted or epoxidized by reacting the haloalkylated polymer with an unsaturated alcohol salt, such as an allyl alcohol salt, in solution, as, for example, described in US Serial No. 08/705,372. Examples of suitable unsaturated alcohol salts and allyl alcohol salts include sodium 2-allylphenolate, sodium 4-allylphenolate, sodium allyl alcoholate, corresponding salts with lithium, potassium, cesium, rubidium, ammonium, quaternary alkyl ammonium compounds, and the like. Unsaturated alcohol salts can be generated by the reaction of the alcohol with a base, such as sodium hydride, sodium hydroxide, or the like. The salt displaces the halide

of the haloalkyl groups at between about 25 and about 100°C. Examples of solvents suitable for the reaction include polar aprotic solvents such as N,N-dimethylacetamide, dimethylsulfoxide, N-methylpyrrolidinone, dimethylformamide, tetrahydrofuran, and the like. Typically, the reactants are present in relative amounts with respect to each other of from about 1 to about 50 molar equivalents of unsaturated alcohol salt per haloalkyl group to be substituted, although the relative amounts can be outside this range. Typically, the reactants are present in solution in amounts of from about 5 to about 50 percent by weight solids, and preferably about 10 percent by weight solids, although the relative amounts can be outside this range.

The haloalkylated polymer can be substituted with a photosensitivity-imparting, water-solubility-enhancing (or water-dispersability-enhancing) group by reacting the haloalkylated polymer with an unsaturated amine, phosphine, or alcohol, as, for example, described in US Serial No. 08/697,760.

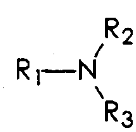
Examples of suitable reactants include N,N-dimethyl ethyl methacrylate, N,N-dimethyl ethyl acrylate,



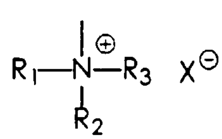


wherein R is H or CH_3 and n is an integer of from 1 to about 50.

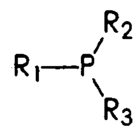
In another embodiment, the polymer of the above formula is substituted with two different functional groups, one of which imparts photosensitivity to the polymer and one of which imparts water solubility or water dispersability to the polymer, as, for example, described in US Serial No. 08/697,760. Either substituent may be placed on the polymer first, followed by the reaction to place the other substituent. In some instances, placement of the photosensitivity-imparting group, such as an unsaturated ester group, first, may be preferred because subsequent measurement of the degree of substitution by the photosensitivity-imparting group may be easier without other substituents, such as water-solubility-imparting groups or water-dispersability-imparting groups, being present. Examples of reactants which can be reacted with the polymer to substitute the polymer with suitable water solubility enhancing groups or water dispersability enhancing groups include tertiary amines of the general formula



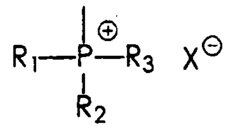
which add to the polymer quaternary ammonium groups of the general formula



wherein R_1, R_2, and R_3 each, independently of the others, can be)but are not limited to) alkyl groups, typically with from 1 to about 30 carbon atoms, substituted alkyl groups, aryl groups, typically with from 6 to about 18 carbon atoms, substituted aryl groups, arylalkyl groups, typically with from 7 to about 19 carbon atoms, and substituted arylalkyl groups, and X represents a halogen atom, such as fluorine, chlorine, bromine, or iodine; tertiary phosphines of the general formula



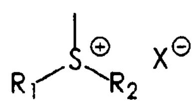
which add to the polymer quaternary phosphonium groups of the general formula



wherein R_1, R_2, and R_3 each, independently of the others, can be (but are not limited to) alkyl groups, typically with from 1 to about 30 carbon atoms, substituted alkyl groups, aryl groups, typically with from 6 to about 18 carbon atoms, substituted aryl groups, arylalkyl groups, typically with from 7 to about 19 carbon atoms, and substituted arylalkyl groups, and X represents a halogen atom, such as fluorine, chlorine, bromine, or iodine; alkyl thio ethers of the general formula

$$R_1—S—R_2$$

which add to the polymer sulfonium groups of the general formula



wherein R_1 and R_2 each, independently of the other, can be (but are not limited to) alkyl groups, typically with from 1 to about 6 carbon atoms and preferably with 1 carbon atom, and substituted alkyl groups, and X represents a halogen atom, such as fluorine, chlorine, bromine, or iodine; wherein the substituents on the substituted alkyl, aryl, and arylalkyl groups can be (but are not limited to) hydroxy groups, amine groups, imine groups, ammonium groups, pyridine groups, pyridinium groups, ether groups, aldehyde groups, ketone groups, ester groups, amide groups, carboxylic acid groups, carbonyl groups, thiocarbonyl groups, sulfate groups, sulfonate groups, sulfide groups, sulfoxide groups, phosphine groups, phosphonium groups, phosphate groups, cyano groups, nitrile groups, mercapto groups, nitroso groups, halogen atoms, nitro groups, sulfone groups, acyl groups, acid anhydride groups, azide groups, mixtures thereof, and the like, wherein two or more substituents can be joined together to form a ring.

The hydroxymethylation of a polymer of the above formula can be accomplished by reacting the polymer in solution with formaldehyde or paraformaldehyde and a base, such as sodium hydroxide, potassium hydroxide, calcium hydroxide, ammonium hydroxide, or tetramethylammonium hydroxide, as, for example, described in US Serial No. 08/705,365.

Polymers of the above formula can also be hydroxyalkylated by first preparing the haloalkylated derivative and then replacing at least some of the haloalkyl groups with hydroxyalkyl groups. For example, the haloalkylated polymer can be hydroxyalkylated by alkaline hydrolysis of the haloalkylated polymer. The hydroxy groups replace the halide atoms in the haloalkyl groups on the polymer; accordingly, the number of carbon atoms in the haloalkyl group generally corresponds to the number of carbon atoms in the hydroxyalkyl group. Examples of suitable reactants include sodium hydroxide, potassium hydroxide, calcium hydroxide, ammonium hydroxide, tetraalkyl ammonium hydroxides, such as tetrabutyl ammonium hydroxide. Examples of solvents suitable for the reaction include 1,1,2,2-tetrachloroethane, methylene chloride, and water. Typically, the reactants are present in relative amounts with respect to each other by weight of about 13.8 parts haloalkylated polymer, about 50 parts solvent, and about 30.6 parts base (containing 23 parts tetrabutylammonium hydroxide in water).

Intermediate derivatives can also be prepared by any suitable or desired process. For example, suitable processes for haloalkylating polymers include reaction of the polymers with formaldehyde and hydrochloric acid, bischloromethyl ether, chloromethyl methyl ether, octylchloromethyl ether, or the like, generally in the presence of a Lewis acid catalyst. Bromination of a methyl group on the polymer can also be accomplished with elemental bromine via a free radical

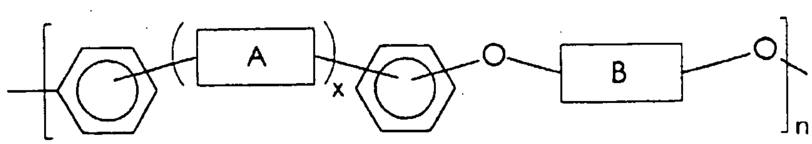
process initiated by, for example, a peroxide initiator or light. Halogen atoms can be substituted for other halogens already on a halomethyl group by, for example, reaction with the appropriate hydrohalic acid or halide salt. Methods for the haloalkylation of polymers are also disclosed in, for example, "Chloromethylation of Condensation Polymers Containing an Oxy-1,4-Phenylene Backbone," W. H. Daly et al., *Polymer Preprints,* Vol. 20, No. 1, 835 (1979).

One specific process suitable for haloalkylating the polymer entails reacting the polymer with an acetyl halide, such as acetyl chloride, and dimethoxymethane in the presence of a halogen-containing Lewis acid catalyst, such as those of the general formula

$$M^{n\oplus} X_n$$

wherein n is an integer of 1, 2, 3, 4, or 5, M represents a boron atom or a metal atom, such as tin, aluminum, zinc, antimony, iron (III), gallium, indium, arsenic, mercury, copper, platinum, palladium, or the like, and X represents a halogen atom, such as fluorine, chlorine, bromine, or iodine, with specific examples including $SnCl_4$, $AlCl_3$, $ZnCl_2$, $AlBr_3$, BF_3, SbF_5, FeI_3, $GaBr_3$, $InCl_3$, AsI_5, $HgBr_2$, CuCl, $PdCl_2$, or $PtBr_2$. A suitable reaction scheme is, for example, described in US Serial No. 08/705,463. Care must be taken to avoid cross-linking of the haloalkylated polymer. Typically, the reactants are present in relative amounts by weight of about 35.3 parts acetyl halide, about 37 parts dimethoxymethane, about 1.2 parts methanol, about 0.3 parts Lewis acid catalyst, about 446 parts 1,1,2,2-tetrachloroethane, and about 10 to 20 parts polymer. 1,1,2,2-Tetrachlorethane is a suitable reaction solvent.

In some instances, the terminal groups on the polymer can be selected by the stoichiometry of the polymer synthesis. For example, when a polymer is prepared by the reaction of 4,4'-dichlorobenzophenone and bis-phenol A in the presence of potassium carbonate in N,N-dimethylacetamide, if the bis-phenol A is present in about 7.5 to 8 mole percent excess, the resulting polymer generally is bis-phenol A-terminated (wherein the bis-phenol A moiety may or may not have one or more hydroxy groups thereon), and the resulting polymer typically has a polydispersity (M_w/M_n) of from about 2 to about 3.5. When the bis-phenol A-terminated polymer is subjected to further reactions to place functional groups thereon, such as haloalkyl groups, and/or to convert one kind of functional group, such as a haloalkyl group, to another kind of functional group, such as an unsaturated ester group, the polydispersity of the polymer can rise to the range of from about 4 to about 6. In contrast, if the 4,4'-dichlorobenzophenone is present in about 7.5 to 8 mole percent excess, the reaction time is approximately half that required for the bis-phenol A excess reaction, the resulting polymer generally is benzophenone-terminated (wherein the benzophenone moiety may or may not have one or more chlorine atoms thereon), and the resulting polymer typically has a polydispersity of from about 2 to about 3.5. When the benzophenone-terminated polymer is subjected to further reactions to place functional groups thereon, such as haloalkyl groups, and/or to convert one kind of functional group, such as a haloalkyl group, to another kind of functional group, such as an unsaturated ester group, the polydispersity of the polymer typically remains in the range of from about 2 to about 3.5. Similarly, when a polymer is prepared by the reaction of 4,4'-difluorobenzophenone with either 9,9'-bis(4-hydroxyphenyl)fluorene or bis-phenol A in the presence of potassium carbonate in N,N-dimethylacetamide, if the 4,4'-difluorobenzophenone reactant is present in excess, the resulting polymer generally has benzophenone terminal groups (which may or may not have one or more fluorine atoms thereon). The well-known Carothers equation can be employed to calculate the stoichiometric offset required to obtain the desired molecular weight. (See, for example, William H. Carothers, "An Introduction to the General Theory of Condensation Polymers," *Chem. Rev.*, ***8***, 353 (1931) and *J. Amer. Chem. Soc.*, ***51***, 2548 (1929); see also P. J. Flory, *Principles of Polymer Chemistry,* Cornell University Press, Ithaca, New York (1953). More generally speaking, during the preparation of polymers of the formula



the stoichiometry of the polymer synthesis reaction can be adjusted so that the end groups of the polymer are derived from the "A" groups or derived from the "B" groups. Specific functional groups can also be present on these terminal "A" groups or "B" groups, such as ethynyl groups or other thermally sensitive groups, hydroxy groups which are attached to the aromatic ring on an "A" or "B" group to form a phenolic moiety, halogen atoms which are attached to the "A" or "B" group, or the like.

Polymers with end groups derived from the "A" group, such as benzophenone groups or halogenated benzophenone groups, may be preferred for some applications because both the syntheses and some of the reactions of these

materials to place substituents thereon may be easier to control and may yield better results with respect to, for example, cost, molecular weight, molecular weight range, and polydispersity (M_w/M_n) compared to polymers with end groups derived from the "B" group, such as bis-phenol A groups (having one or more hydroxy groups on the aromatic rings thereof) or other phenolic groups. While not being limited to any particular theory, it is believed that the haloalkylation reaction in particular proceeds most rapidly on the phenolic tails when the polymer is bis-phenol A terminated. Moreover, it is believed that halomethylated groups on phenolic-terminated polymers may be particularly reactive to subsequent crosslinking or chain extension. In contrast, it is generally believed that halomethylation does not take place on the terminal aromatic groups with electron withdrawing substituents, such as benzophenone, halogenated benzophenone, or the like. The "A" group terminated materials may also function as an adhesive, and in applications such as thermal ink jet printheads, the use of the crosslinked "A" group terminated polymer may reduce or eliminate the need for an epoxy adhesive to bond the heater plate to the channel plate.

The precise degree of photosensitivity-imparting group substitution of the polymer may be difficult to control, and different batches of photosensitivity-imparting group substituted polymers may have somewhat different degrees of substitution even though the batches were prepared under similar conditions. Photoresist compositions containing polymers for which the degree of photosensitivity-imparting group substitution varies will exhibit variation in characteristics such as photospeed, imaging energy requirements, photosensitivity, shelf life, film forming characteristics, development characteristics, and the like. Accordingly, the photoresist composition containing the photosensitivity-imparting group substituted polymer is prepared according to the present invention.

The first photosensitivity-imparting group substituted polymer can be prepared as described hereinabove. In one embodiment of the present invention, the second component is a polymer which either is substituted with photosensitivity-imparting groups but to a lesser degree than the first polymer, or which does not contain photosensitivity-imparting group substituents. The second polymer may be selected from a wide variety of polymers. For example, in one embodiment of the present invention, two different photosensitivity-imparting group substituted polymers are blended together, wherein one has a higher degree of substitution than the other. In another embodiment of the present invention, the second polymer is a polymer of the above general formula but having no photosensitivity-imparting group substituents, such as the polymer starting materials (and, if deep ultraviolet, x-ray, or electron beam radiation are not being used for photoexposure, the haloalkylated polymers prepared as described hereinabove). In yet another embodiment of the present invention, the second polymer is not necessarily a polymer of the above general formula, but is selected from any of a wide variety of other high performance polymers suitable for obtaining a desirable photoresist mixture with the desired characteristics, such as epoxies, polycarbonates, diallyl phthalates, chloromethylated bisfluorenones, polyphenylenes, phenoxy resins, polyarylene ethers, poly (ether imides), polyarylene ether ketones, polyphenylene sulfides, polysulfones, poly (ether sulfones), polyphenyl triazines, polyimides, polyphenyl quinoxalines, other polyheterocyclic systems, and the like, as well as mixtures thereof. High performance polymers typically are moldable at temperatures above those at which their use is intended, and are useful for high temperature structural applications. While most high performance polymers are thermoplastic, some, such as phenolics, tend to be thermosetting. Any combination of photosensitivity-imparting group substituted polymers of the above formula, polymers having no photosensitivity-imparting group substituents but falling within the above general formula, and/or other polymers outside the scope of the above general formula can be used as the second polymer for the present invention. For example, in one embodiment of the present invention, a photoresist is prepared from: (a) 60 parts by weight of a polyarylene ether ketone within the above general formula having 1 chloromethyl group per repeating monomer unit, 1 acrylate group per repeating monomer unit, and a number average molecular weight of 60,000; (b) 40 parts by weight of a polyarylene ether ketone resin within the above general formula but having no substituents thereon, with a number average molecular weight of 2,800 and a polydispersity (M_w/M_n) of about 2.5; and (c) 10 parts by weight of EPON 1001 adhesive resin (Shell Chemical Company, Houston, TX). This mixture has a degree of acryloylation of about 1.1 milliequivalents of acrylate per gram of resin solids and a weight average molecular weight of 34,000. Typically, when a photoresist is prepared from a mixture of an unsaturated ester substituted polymer of the above general formula and a second polymer having no unsaturated ester groups, a photoresist solution containing about 40 percent by weight polymer solids will contain from 10 to about 25 parts by weight of a polymer having unsaturated ester substituents and from about 10 to about 25 parts by weight of a polymer having no unsaturated ester substituents.

In still another embodiment of the present invention, the second component is a reactive diluent. In some embodiments, the reactive diluent is a liquid, and can replace a solvent when the photopatternable polymer is too high in viscosity to be cured without solvents. In other embodiments, the reactive diluent is a solid. The reactive diluent has functional groups which are capable of polymerizing when the reactive diluent is exposed to actinic radiation at an energy or wavelength level which is capable of inducing crosslinking or chain extension in the photopatternable polymer. Reactive diluents preferably are monomeric or oligomeric, and include (but are not limited to) mono-, di-, tri-, and multifunctional unsaturated ester monomers and the like. Examples of suitable reactive diluents include monoacrylates, such as cyclohexyl acrylate, 2-ethoxy ethyl acrylate, 2-methoxy ethyl acrylate, 2(2-ethoxyethoxy) ethyl acrylate, stearyl acrylate, tetrahydrofurfuryl acrylate, octyl acrylate, lauryl acrylate, behenyl acrylate, 2-phenoxy ethyl acrylate, tertiary

butyl acrylate, glycidyl acrylate, isodecyl acrylate, benzyl acrylate, hexyl acrylate, isooctyl acrylate, isobornyl acrylate, butanediol monoacrylate, ethoxylated phenol monoacrylate, oxyethylated phenol acrylate, monomethoxy hexanediol acrylate, β-carboxy ethyl acrylate, dicyclopentyl acrylate, carbonyl acrylate, octyl decyl acrylate, ethoxylated nonylphenol acrylate, hydroxyethyl acrylate, hydroxyethyl methacrylate, and the like, diacrylates, such as 1,3-butylene glycol diacrylate, 1,4-butanediol diacrylate, diethylene glycol diacrylate, 1,6-hexanediol diacrylate, tetraethylene glycol diacrylate, triethylene glycol diacrylate, tripropylene glycol diacrylate, polybutanediol diacrylate, polyethylene glycol diacrylate, propoxylated neopentyl glycol diacrylate, ethoxylated neopentyl glycol diacrylate, polybutadiene diacrylate, and the like, polyacrylates, such as trimethylol propane triacrylate, pentaerythritol tetraacrylate, pentaerythritol triacrylate, dipentaerythritol pentaacrylate, glycerol propoxy triacrylate, tris(2-hydroxyethyl) isocyanurate triacrylate, pentaacrylate ester, and the like, epoxy acrylates, polyester acrylates, polyether polyol acrylates, urethane acrylates, amine acrylates, acrylic acrylates, and the like. Mixtures of two or more materials can also be employed as the reactive diluent. Suitable reactive diluents are commercially available from, for example, Sartomer Co., Inc., Henkel Corp., Radcure Specialties, and the like. When the second component is a reactive diluent, typically, the first and second components are present in relative amounts of from about 5 to about 50 percent by weight reactive diluent (second component) and from about 50 to about 95 percent by weight polymer (first component), and preferably in relative amounts of from about 10 to about 20 percent by weight reactive diluent (second component) and from about 80 to about 90 percent by weight polymer (first component), although the relative amounts can be outside these ranges.

The blend containing the first and second components typically has a weight average molecular weight of from about 10,000 to about 50,000, preferably from about 10,000 to about 35,000, and more preferably from about 10,000 to about 25,000, although the weight average molecular weight of the blend can be outside these ranges. The blend containing the first and second components typically has a degree of photosensitivity-imparting-group substitution of from about 0.25 to about 2 milliequivalents of photosensitivity-imparting group per gram of mixture, preferably from about 0.8 to about 1.4 milliequivalents per gram of mixture, although the degree of substitution can be outside these ranges.

The photopatternable polymer can be cured by uniform exposure to actinic radiation at wavelengths and/or energy levels capable of causing crosslinking or chain extension of the polymer through the photosensitivity-imparting groups. Alternatively, the photopatternable polymer is developed by imagewise exposure of the material to radiation at a wavelength and/or at an energy level to which the photosensitivity-imparting groups are sensitive. Typically, a photoresist composition will contain the photopatternable polymer, an optional solvent for the photopatternable polymer, an optional sensitizer, and an optional photoinitiator. Solvents may be particularly desirable when the uncrosslinked photopatternable polymer has a high T_g. The solvent and photopatternable polymer typically are present in relative amounts of from 0 to about 99 percent by weight solvent and from about 1 to 100 percent polymer, preferably are present in relative amounts of from about 20 to about 60 percent by weight solvent and from about 40 to about 80 percent by weight polymer, and more preferably are present in relative amounts of from about 30 to about 60 percent by weight solvent and from about 40 to about 70 percent by weight polymer, although the relative amounts can be outside these ranges.

Sensitizers absorb light energy and facilitate the transfer of energy to unsaturated bonds which can then react to crosslink or chain extend the resin. Sensitizers frequently expand the useful energy wavelength range for photoexposure, and typically are aromatic light absorbing chromophores. Sensitizers can also lead to the formation of photoinitiators, which can be free radical or ionic. When present, the optional sensitizer and the photopatternable polymer typically are present in relative amounts of from about 0.1 to about 20 percent by weight sensitizer and from about 80 to about 99.9 percent by weight photopatternable polymer, and preferably are present in relative amounts of from about 1 to about 10 percent by weight sensitizer and from about 90 to about 99 percent by weight photopatternable polymer, although the relative amounts can be outside these ranges.

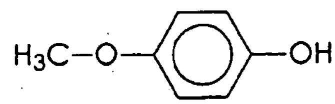
Photoinitiators generally generate ions or free radicals which initiate polymerization upon exposure to actinic radiation. When present, the optional photoinitiator and the photopatternable polymer typically are present in relative amounts of from about 0.1 to about 20 percent by weight photoinitiator and from about 80 to about 99.9 percent by weight photopatternable polymer, and preferably are present in relative amounts of from about 1 to about 10 percent by weight photoinitiator and from about 90 to about 99 percent by weight photopatternable polymer, although the relative amounts can be outside these ranges.

A single material can also function as both a sensitizer and a photoinitiator.

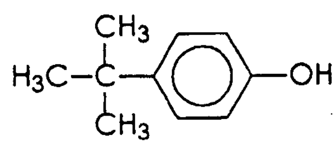
Examples of specific sensitizers and photoinitiators include Michler's ketone (Aldrich Chemical Co.), Darocure 1173, Darocure 4265, Irgacure 184, Irgacure 261, and Irgacure 907 (available from Ciba-Geigy, Ardsley, New York), and mixtures thereof. Further background material on initiators is disclosed in, for example, Ober et al., *J.M.S. - Pure Appl. Chem.*, **A30** (12), 877-897 (1993); G. E. Green, B. P. Stark, and S. A. Zahir, "Photocrosslinkable Resin Systems, " *J. Macro. Sci. -- Revs. Macro. Chem.*, C21(2), 187 (1981); H. F. Gruber, "Photoinitiators for Free Radical Polymerization," *Prog. Polym. Sci.*, Vol. 17, 953 (1992); Johann G. Kloosterboer, "Network Formation by Chain Crosslinking Photopolymerization and Its Applications in Electronics," *Advances in Polymer Science, **89***, Springer-Verlag Berlin Heidelberg (1988); and "Diaryliodonium Salts as Thermal Initiators of Cationic Polymerization," J. V. Crivello, T.P. Lock-

hart, and J. L. Lee, J. *of Polymer Science: Polymer Chemistry Edition,* ***21,*** 97 (1983). Sensitizers are available from, for example, Aldrich Chemical Co., Milwaukee, WI, and Pfaltz and Bauer, Waterberry, CT. Benzophenone and its derivatives can function as photosensitizers. Triphenylsulfonium and diphenyl iodonium salts are examples of typical cationic photoinitiators.

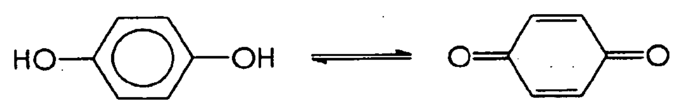
Inhibitors may also optionally be present in the photoresist containing the photopatternable polymer. Examples of suitable inhibitors include MEHQ, a methyl ether of hydroquinone, of the formula



t-butylcatechol, of the formula

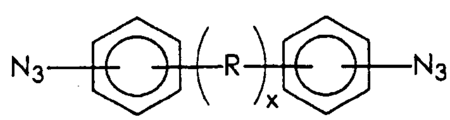


hydroquinone, of the formula

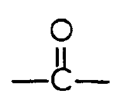


and the like, the inhibitor typically present in an amount of from about 500 to about 1,500 parts per million by weight of a photoresist solution containing about 40 percent by weight polymer solids, although the amount can be outside this range.

One specific example of a class of suitable sensitizers or initiators is that of bis(azides), of. the general formula



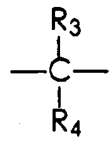
wherein R is



,

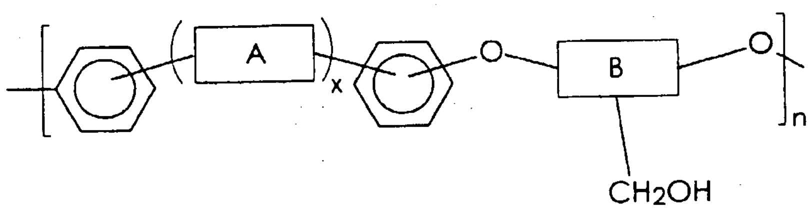
$-R_1C=CR_2-$,

or

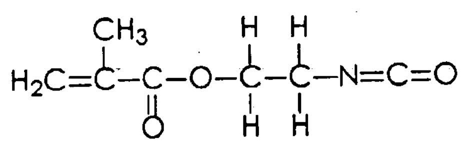


wherein R_1, R_2, R_3, and R_4 each, independently of the others, is a hydrogen atom, an alkyl group, including saturated, unsaturated, and cyclic alkyl groups, preferably with from 1 to about 30 carbon atoms, and more preferably with from 1 to about 6 carbon atoms, a substituted alkyl group, an aryl group, preferably with from 6 to about 18 carbon atoms, and more preferably with about 6 carbon atoms, a substituted aryl group, an arylalkyl group, preferably with from 7 to about 48 carbon atoms, and more preferably with from about 7 to about 8 carbon atoms, or a substituted arylalkyl group, and x is 0 or 1.

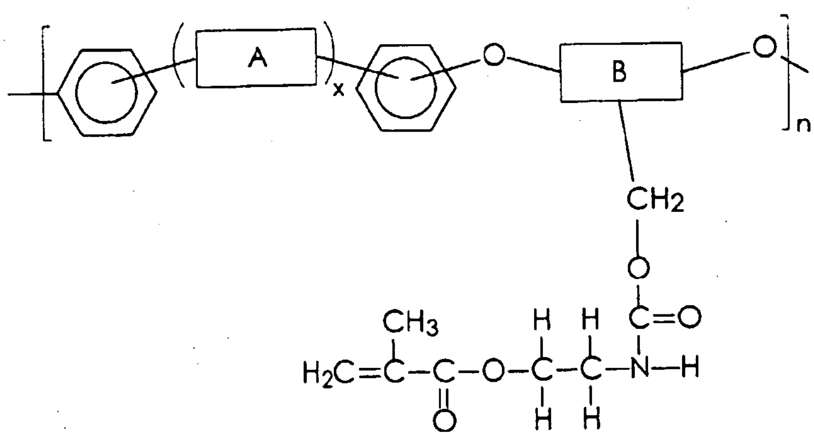
A hydroxyalkylated polymer can be further reacted to render it more photosensitive. For example, a hydroxymethylated polymer of the formula



can react with isocyanato-ethyl methacrylate, of the formula



(available from Polysciences, Warrington, PA) to form a photoactive polymer of the formula

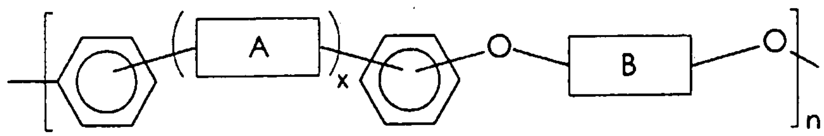


This reaction can be carried out in methylene chloride at 25°C with 1 part by weight polymer, 1 part by weight isocyanato-ethyl methacrylate, and 50 parts by weight methylene chloride. Typical reaction temperatures are from about 0 to about 50°C, with 10 to 25°C preferred. Typical reaction times are between about 1 and about 24 hours, with about 16 hours preferred. During exposure to, for example, ultraviolet radiation, the ethylenic bond opens and crosslinking or chain

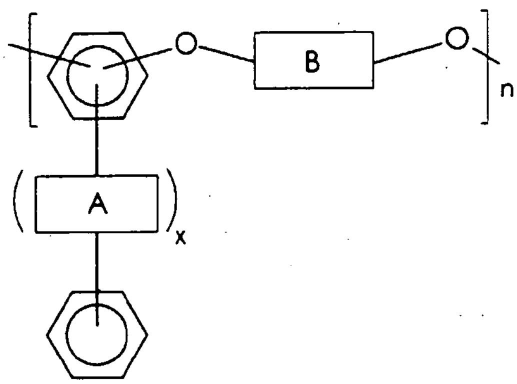
extension occurs at that site.

Many of the photosensitivity-imparting groups which are indicated above as being capable of enabling crosslinking or chain extension of the polymer upon exposure to actinic radiation can also enable crosslinking or chain extension of the polymer upon exposure to elevated temperatures; thus the polymers of the present invention can also, if desired, be used in applications wherein thermal curing is employed.

In all of the above reactions and substitutions illustrated above for the polymer of the formula



it is to be understood that analogous reactions and substitutions will occur for the polymer of the formula



Photopatternable polymers prepared by the process of the present invention can be used as components in ink jet printheads. The printheads of the present invention can be of any suitable configuration. An example of a suitable configuration, suitable in this instance for thermal ink jet printing, is illustrated schematically in Figure 1, which depicts an enlarged, schematic isometric view of the front face 29 of a printhead 10 showing the array of droplet emitting nozzles 27. Referring also to Figure 2, discussed later, the lower electrically insulating substrate or heating element plate 28 has the heating elements 34 and addressing electrodes 33 patterned on surface 30 thereof, while the upper substrate or channel plate 31 has parallel grooves 20 which extend in one direction and penetrate through the upper substrate front face edge 29. The other end of grooves 20 terminate at slanted wall 21, the floor 41 of the internal recess 24 which is used as the ink supply manifold for the capillary filled ink channels 20, has an opening 25 there-through for use as an ink fill hole. The surface of the channel plate with the grooves are aligned and bonded to the heater plate 28, so that a respective one of the plurality of heating elements 34 is positioned in each channel, formed by the grooves and the lower substrate or heater plate. Ink enters the manifold formed by the recess 24 and the lower substrate 28 through the fill hole 25 and by capillary action, fills the channels 20 by flowing through an elongated recess 38 formed in the thick film insulative layer 18. The ink at each nozzle forms a meniscus, the surface tension of which prevents the ink from weeping therefrom. The addressing electrodes 33 on the lower substrate or channel plate 28 terminate at terminals 32. The upper substrate or channel plate 31 is smaller than that of the lower substrate in order that the electrode terminals 32 are exposed and available for wire bonding to the electrodes on the daughter board 19, on which the printhead 10 is permanently mounted. Layer 18 is a thick film passivation layer, discussed later, sandwiched between the upper and lower substrates. This layer is etched to expose the heating elements, thus placing them in a pit, and is etched to form the elongated recess to enable ink flow between the manifold 24 and the ink channels 20. In addition, the thick film insulative layer is etched to expose the electrode terminals.

A cross sectional view of Figure 1 is taken along view line 2-2 through one channel and shown as Figure 2 to show how the ink flows from the manifold 24 and around the end 21 of the groove 20 as depicted by arrow 23. As is disclosed in U.S. Patent 4,638,337, U.S. Patent 4,601,777, and U.S. Patent Re. 32,572, a plurality of sets of bubble generating heating elements 34 and their addressing electrodes 33 can be patterned on the polished surface of a single side polished (100) silicon wafer. Prior to patterning, the multiple sets of printhead electrodes 33, the resistive material that serves as the heating elements 34, and the common return 35, the polished surface of the wafer is coated with an underglaze layer 39 such as silicon dioxide, having a typical thickness of from about 500nm (5,000 Angstroms) to

about 2 micrometers (microns), although the thickness can be outside this range. The resistive material can be a doped polycrystalline silicon, which can be deposited by chemical vapor deposition (CVD) or any other well known resistive material such as zirconium boride (ZrB_2). The common return and the addressing electrodes are typically aluminum leads deposited on the underglaze and over the edges of the heating elements. The common return ends or terminals 37 and addressing electrode terminals 32 are positioned at predetermined locations to allow clearance for wire bonding to the electrodes (not shown) of the daughter board 19, after the channel plate 31 is attached to make a printhead. The common return 35 and the addressing electrodes 33 are deposited to a thickness typically of from about 0.5 to about 3 micrometers (microns), although the thickness can be outside this range, with the preferred thickness being 1.5 micrometers (microns).

If polysilicon heating elements are used, they may be subsequently oxidized in steam or oxygen at a relatively high temperature, typically about 1,100°C although the temperature can be above or below this value, for a period of time typically of from about 50 to about 80 minutes, although the time period can be outside this range, prior to the deposition of the aluminum leads, in order to convert a small portion of the polysilicon to SiO_2. In such cases, the heating elements are thermally oxidized to achieve an overglaze (not shown) of SiO_2 with a thickness typically of from about 50nm (500 Angstroms) to about 1 micrometer (micron), although the thickness can be outside this range, which has good integrity with substantially no pinholes.

In one embodiment, polysilicon heating elements are used and an optional silicon dioxide thermal oxide layer 17 is grown from the polysilicon in high temperature steam. The thermal oxide layer is typically grown to a thickness of from about 0.5 to about 1 micrometer (micron), although the thickness can be outside this range, to protect and insulate the heating elements from the conductive ink. The thermal oxide is removed at the edges of the polysilicon heating elements for attachment of the addressing electrodes and common return, which are then patterned and deposited. If a resistive material such as zirconium boride is used for the heating elements, then other suitable well known insulative materials can be used for the protective layer thereover. Before electrode passivation, a tantalum (Ta) layer (not shown) can be optionally deposited, typically to a thickness of about 1 micron, although the thickness can be above or below this value, on the heating element protective layer 17 for added protection thereof against the cavitational forces generated by the collapsing ink vapor bubbles during printhead operation. The tantalum layer is etched off all but the protective layer 17 directly over the heating elements using, for example, CF_4/O_2 plasma etching. For polysilicon heating elements, the aluminum common return and addressing electrodes typically are deposited on the underglaze layer and over the opposing edges of the polysilicon heating elements which have been cleared of oxide for the attachment of the common return and electrodes.

For electrode passivation, a film 16 is deposited over the entire wafer surface, including the plurality of sets of heating elements and addressing electrodes. The passivation film 16 provides an ion barrier which will protect the exposed electrodes from the ink. Examples of suitable ion barrier materials for passivation film 16 include polyimide, plasma nitride, phosphorous doped silicon dioxide, materials disclosed herein as being suitable for insulative layer 18, as well as any combinations thereof. An effective ion barrier layer is generally achieved when its thickness is from about 100nm (1000 Angstroms) to about 10 micrometers (microns), although the thickness can be outside this range. In 300 dpi printheads, passivation layer 16 preferably has a thickness of about 3 microns, although the thickness can be above or below this value. In 600 dpi printheads, the thickness of passivation layer 16 preferably is such that the combined thickness of layer 16 and layer 18 is about 25 micrometers (microns), although the thickness can be above or below this value. The passivation film or layer 16 is etched off of the terminal ends of the common return and addressing electrodes for wire bonding later with the daughter board electrodes. This etching of the silicon dioxide film can be by either the wet or dry etching method. Alternatively, the electrode passivation can be by plasma deposited silicon nitride (Si_3N_4).

Next, a thick film type insulative layer 18, of a polymeric material discussed in further detail herein, is formed on the passivation layer 16, typically having a thickness of from about 10 to about 100 micrometers (microns) and preferably in the range of from about 25 to about 50 microns, although the thickness can be outside these ranges. Even more preferably, in 300 dpi printheads, layer 18 preferably has a thickness of about 30 micrometers (microns), and in 600 dpi printheads, layer 18 preferably has a thickness of from about 20 to about 22 micrometers (microns), although other thicknesses can be employed. The insulative layer 18 is photolithographically processed to enable etching and removal of those portions of the layer 18 over each heating element (forming recesses 26), the elongated recess 38 for providing ink passage from the manifold 24 to the ink channels 20, and over each electrode terminal 32, 37. The elongated recess 38 is formed by the removal of this portion of the thick film layer 18. Thus, the passivation layer 16 alone protects the electrodes 33 from exposure to the ink in this elongated recess 38. Optionally, if desired, insulative layer 18 can be applied as a series of thin layers of either similar or different composition. Typically, a thin layer is deposited, photoexposed, partially cured, followed by deposition of the next thin layer, photoexposure, partial curing, and the like. The thin layers constituting thick film insulative layer 18 contain a polymer of the formula indicated hereinabove. In one embodiment of the present invention, a first thin layer is applied to contact layer 16, said first thin layer containing a mixture of a polymer of the formula indicated hereinabove and an epoxy polymer, followed by photoex-

posure, partial curing, and subsequent application of one or more successive thin layers containing a polymer of the formula indicated hereinabove.

Figure 3 is a similar view to that of Figure 2 with a shallow anisotropically etched groove 40 in the heater plate, which is silicon, prior to formation of the underglaze 39 and patterning of the heating elements 34, electrodes 33 and common return 35. This recess 40 permits the use of only the thick film insulative layer 18 and eliminates the need for the usual electrode passivating layer 16. Since the thick film layer 18 is impervious to water and relatively thick (typically from about 20 to about 40 microns, although the thickness can be outside this range), contamination introduced into the circuitry will be much less than with only the relatively thin passivation layer 16 well known in the art. The heater plate is a fairly hostile environment for integrated circuits. Commercial ink generally entails a low attention to purity. As a result, the active part of the heater plate will be at elevated temperature adjacent to a contaminated aqueous ink solution which undoubtedly abounds with mobile ions. In addition, it is generally desirable to run the heater plate at a voltage of from about 30 to about 50 volts, so that there will be a substantial field present. Thus, the thick film insulative layer 18 provides improved protection for the active devices and provides improved protection, resulting in longer operating lifetime for the heater plate.

When a plurality of lower substrates 28 are produced from a single silicon wafer, at a convenient point after the underglaze is deposited, at least two alignment markings (not shown) preferably are photolithographically produced at predetermined locations on the lower substrates 28 which make up the silicon wafer. These alignment markings are used for alignment of the plurality of upper substrates 31 containing the ink channels. The surface of the single sided wafer containing the plurality of sets of heating elements is bonded to the surface of the wafer containing the plurality of ink channel containing upper substrates subsequent to alignment.

As disclosed in U.S. Patent 4,601,777 and U.S. Patent 4,638,337, the channel plate is formed from a two side polished, (100) silicon wafer to produce a plurality of upper substrates 31 for the printhead. After the wafer is chemically cleaned, a pyrolytic CVD silicon nitride layer (not shown) is deposited on both sides. Using conventional photolithography, a via for fill hole 25 for each of the plurality of channel plates 31 and at least two vias for alignment openings (not shown) at predetermined locations are printed on one wafer side. The silicon nitride is plasma etched off of the patterned vias representing the fill holes and alignment openings. A potassium hydroxide (KOH) anisotropic etch can be used to etch the fill holes and alignment openings. In this case, the [111] planes of the (100) wafer typically make an angle of about 54.7 degrees with the surface of the wafer. The fill holes are small square surface patterns, generally of about 20 mils (500 microns) per side, although the dimensions can be above or below this value, and the alignment openings are from about 60 to about 80 mils (1.5 to 3 millimeters) square, although the dimensions can be outside this range. Thus, the alignment openings are etched entirely through the 20 mil (0.5 millimeter) thick wafer, while the fill holes are etched to a terminating apex at about halfway through to three-quarters through the wafer. The relatively small square fill hole is invariant to further size increase with continued etching so that the etching of the alignment openings and fill holes are not significantly time constrained.

Next, the opposite side of the wafer is photolithographically patterned, using the previously etched alignment holes as a reference to form the relatively large rectangular recesses 24 and sets of elongated, parallel channel recesses that will eventually become the ink manifolds and channels of the printheads. The surface 22 of the wafer containing the manifold and channel recesses are portions of the original wafer surface (covered by a silicon nitride layer) on which an adhesive, such as a thermosetting epoxy, will be applied later for bonding it to the substrate containing the plurality of sets of heating elements. The adhesive is applied in a manner such that it does not run or spread into the grooves or other recesses. The alignment markings can be used with, for example, a vacuum chuck mask aligner to align the channel wafer on the heating element and addressing electrode wafer. The two wafers are accurately mated and can be tacked together by partial curing of the adhesive. Alternatively, the heating element and channel wafers can be given precisely diced edges and then manually or automatically aligned in a precision jig. Alignment can also be performed with an infrared aligner-bonder, with an infrared microscope using infrared opaque markings on each wafer to be aligned, or the like. The two wafers can then be cured in an oven or laminator to bond them together permanently. The channel wafer can then be milled to produce individual upper substrates. A final dicing cut, which produces end face 29, opens one end of the elongated groove 20 producing nozzles 27. The other ends of the channel groove 20 remain closed by end 21. However, the alignment and bonding of the channel plate to the heater plate places the ends 21 of channels 20 directly over elongated recess 38 in the thick film insulative layer 18 as shown in Figure 2 or directly above the recess 40 as shown in Figure 3 enabling the flow of ink into the channels from the manifold as depicted by arrows 23. The plurality of individual printheads produced by the final dicing are bonded to the daughter board and the printhead electrode terminals are wire bonded to the daughter board electrodes.

In one embodiment, a heater wafer with a phosphosilicate glass layer is spin coated with a solution of Z6020 adhesion promoter (0.01 weight percent in 95 parts methanol and 5 parts water, Dow Corning) at 3000 revolutions per minute for 10 seconds and dried at 100°C for between 2 and 10 minutes. The wafer is then allowed to cool at 25°C for 5 minutes before spin coating the photoresist onto the wafer at between 1,000 and 3,000 revolutions per minute for between 30 and 60 seconds. The photoresist solution is made by dissolving polyarylene ether ketone with 0.75

acryloyl groups and 0.75 chloromethyl groups per repeat unit and a weight average molecular weight of 25,000 in N-methylpyrrolidinone at 40 weight percent solids with Michler's ketone (1.2 parts ketone per every 10 parts of 40 weight percent solids polymer solution). The film is heated (soft baked) in an oven for between 10 and 15 minutes at 70°C. After cooling to 25°C over 5 minutes, the film is covered with a mask and exposed to 365 nanometer ultraviolet light, amounting to between 150 and 1,500 milliJoules per cm^2. The exposed wafer is then heated at 70°C for 2 minutes post exposure bake, followed by cooling to 25°C over 5 minutes. The film is developed with 60:40 chloroform/cyclohexanone developer, washed with 90:10 hexanes/cyclohexanone, and then dried at 70°C for 2 minutes. A second developer/wash cycle is carried out if necessary to obtain a wafer with clean features. The processed wafer is transferred to an oven at 25°C, and the oven temperature is raised from 25 to 90°C at 2°C per minute. The temperature is maintained at 90°C for 2 hours, and then increased to 260°C at 2°C per minute. The oven temperature is maintained at 260°C for 2 hours and then the oven is turned off and the temperature is allowed to cool gradually to 25°C. When thermal cure of the photoresist films is carried out under inert atmosphere, such as nitrogen or one of the noble gases, such as argon, neon, krypton, xenon, or the like, there is markedly reduced oxidation of the developed film and improved thermal and hydrolytic stability of the resultant devices. Moreover, adhesion of developed photoresist film is improved to the underlying substrate. If a second layer is spin coated over the first layer, the heat cure of the first developed layer can be stopped between 80 and 260°C before the second layer is spin coated onto the first layer. A second thicker layer is deposited by repeating the above procedure a second time. This process is intended to be a guide in that procedures can be outside the specified conditions depending on film thickness and photoresist molecular weight. Films at 30 microns have been developed with clean features at 600 dots per inch.

In a particularly preferred embodiment, the photopatternable polymer is admixed with an epoxy resin in relative amounts of from about 75 parts by weight photopatternable polymer and about 25 parts by weight epoxy resin to about 90 parts by weight photopatternable polymer and about 10 parts by weight epoxy resin.

The present invention also encompasses printing processes with printheads according to the present invention. One embodiment of the present invention is directed to an ink jet printing process which comprises (1) preparing an ink jet printhead comprising a plurality of channels, wherein the channels are capable of being filled with ink from an ink supply and wherein the channels terminate in nozzles on one surface of the printhead, said preparation being according to the process of the present invention; (2) filling the channels with an ink; and (3) causing droplets of ink to be expelled from the nozzles onto a receiver sheet in an image pattern. A specific embodiment of this process is directed to a thermal ink jet printing process, wherein the droplets of ink are caused to be expelled from the nozzles by heating selected channels in an image pattern. The droplets can be expelled onto any suitable receiver sheet, such as fabric, plain paper such as Xerox® 4024 or 4010, coated papers, ro transparency materials.

All parts and percentages in the Examples are by weight unless otherwise indicated.

EXAMPLE I

A first acryloylated polyarylene ether ketone resin having 1 acrylate group per repeating monomer unit and one chloromethyl group per repeating monomer unit and having a weight average molecular weight of about 60,000 was prepared as follows. A 1 liter, 3-neck round-bottom flask equipped with a Dean-Stark (Barrett) trap, condenser, mechanical stirrer, argon inlet, and stopper was situated in a silicone oil bath. 4,4'-Dichlorobenzophenone (Aldrich 11,370, Aldrich Chemical Co., Milwaukee, WI, 50 grams), bis-phenol A (Aldrich 23,965-8, 48.96 grams), potassium carbonate (65.56 grams), anhydrous *N,N*-dimethylacetamide (300 milliliters), and toluene (55 milliliters) were added to the flask and heated to 175°C (oil bath temperature) while the volatile toluene component was collected and removed. After 48 hours of heating at 175°C with continuous stirring, the reaction mixture was filtered to remove potassium carbonate and precipitated into methanol (2 gallons). The polymer (poly(4-CPK-BPA)) was isolated after filtration and drying *in vacuo*. Gel permeation chromatography (gpc) (elution solvent was tetrahydrofuran) analysis was as follows: M_n 3,360, M_{peak} 9,139, M_w 5,875, M_z 19,328, and M_{z+1} 29,739. Solution cast films from methylene chloride were clear, tough, and flexible. As a result of the stoichiometries used in the reaction, it is believed that this polymer had end groups derived from bis-phenol A. The polymer thus prepared was chloromethylated as follows. A solution of chloromethyl ether in methyl acetate was made by adding 282.68 grams (256 milliliters) of acetyl chloride to a mixture of dimethoxy methane (313.6 grams, 366.8 milliliters) and methanol (10 milliliters) in a 5 liter 3-neck round-bottom flask equipped with a mechanical stirrer, argon inlet, reflux condenser, and addition funnel. The solution was diluted with 1,066.8 milliliters of 1,1,2,2-tetrachloroethane and then tin tetrachloride (2.4 milliliters) was added via a gas-tight syringe along with 1,1,2,2-tetrachloroethane (133.2 milliliters) using an addition funnel. The reaction solution was heated to 500°C. Thereafter, a solution of the poly(4-CPK-BPA) (160.8 grams) in 1,000 milliliters of tetrachloroethane was added rapidly. The reaction mixture was then heated to reflux with an oil bath set at 110°C. After 4 hours reflux with continuous stirring, heating was discontinued and the mixture was allowed to cool to 25°C. The reaction mixture was transferred in stages to a 2 liter round bottom flask and concentrated using a rotary evaporator with gentle heating up to 50°C while reduced pressure was maintained with a vacuum pump trapped with liquid nitrogen. The concentrate was added to methanol

(4 gallons) to precipitate the polymer using a Waring blender. The polymer was isolated by filtration and vacuum dried to yield poly(4-CPK-BPA) with 2 chloromethyl groups per repeat unit as identified using ^{1}H NMR spectroscopy. Solvent free polymer was obtained by reprecipitation of the polymer (75 grams) in methylene chloride (500 grams) into methanol (3 gallons) followed by filtration and vacuum drying to yield solvent free polymer. Gel permeation chromatography (gpc) (elution solvent was tetrahydrofuran) analysis was as follows: M_n 4,527, M_{peak} 12,964, M_w 12,179, M_z 21,824, and M_{z+1} 30,612. The chloromethylated polymer was then acryloylated as follows. A solution was prepared containing 90 grams of the chloromethylated polymer with 2 chloromethyl groups per repeat unit in 639 milliliters (558.5 grams) of *N,N*-dimethylacetamide and the solution was magnetically stirred at 25°C with sodium acrylate (51.39 grams) for 1 week. The reaction mixture was then centrifuged, and the supernate was added to methanol (4.8 gallons) using a Waring blender in relative amounts of 25 milliliters of polymer solution per 0.75 liter of methanol. The white powder that precipitated was filtered, and the wet filter cake was washed with water (3 gallons) and then methanol (3 gallons). The polymer was then isolated by filtration and vacuum dried to yield a white powder. The polymer had 1 acrylate group for every repeating monomer unit and 1 chloromethyl groups for every repeating monomer unit. Gel permeation chromatography (gpc) (elution solvent was tetrahydrofuran) analysis was as follows: M_n 10,922, M_{peak} 24,895, M_w 62,933, M_z 210,546, and M_{z+1} 411,394.

A second acryloylated polyarylene ether ketone resin with a weight average molecular weight of about 8,000 and having 1 acrylate group per every eight repeating monomer units and 1 chloromethyl group per every eight repeating monomer units was prepared as follows. A 1 liter, 3-neck round-bottom flask equipped with a Dean-Stark (Barrett) trap, condenser, mechanical stirrer, argon inlet, and stopper was situated in a silicone oil bath. 4,4'-Dichlorobenzophenone (Aldrich 11,370, Aldrich Chemical Co., Milwaukee, WI, 50 grams), bis-phenol A (Aldrich 23,965-8, 48.96 grams), potassium carbonate (65.56 grams), anhydrous *N,N*-dimethylacetamide (300 milliliters), and toluene (55 milliliters) were added to the flask and heated to 175°C (oil bath temperature) while the volatile toluene component was collected and removed. After 24 hours of heating at 175°C with continuous stirring, an aliquot of the reaction product that had been precipitated into methanol was analyzed by gel permeation chromatography (gpc) (elution solvent was tetrahydrofuran) with the following results: M_n 4464, M_{peak} 7583, M_w 7927, M_z 12,331, and M_{z+1} 16,980. As a result of the stoichiometries used in the reaction, it is believed that this polymer had end groups derived from bis-phenol A. This polymer contained 7 mol% N,N-dimethylacetamide as residual solvent. When the residual N,N-dimethylacetamide exceeds 5 mol% of the polymer, the chloromethylation reaction of the next step proceeds only to a maximum value of 1 chloromethyl group per every 4 monomer repeat units. A solution of chloromethyl ether in methyl acetate was made by adding 35.3 grams of acetyl chloride to a mixture of dimethoxy methane (45 milliliters) and methanol (1.25 milliliters) in a 500 milliliter 3-neck round-bottom flask equipped with a mechanical stirrer, argon inlet, reflux condenser, and addition funnel. The solution was diluted with 150 milliliters of 1,1,2,2-tetrachloroethane and then tin tetrachloride (0.3 milliliters) was added via syringe. The solution was heated to reflux with an oil bath set at 110°C. Thereafter, a solution of the poly(4-CPK-BPA) containing residual solvent (10 grams of polymer) in 125 milliliters of 1,1,2,2-tetrachloroethane was added over 8 minutes. After two hours reflux with continuous stirring, heating was discontinued and the mixture was allowed to cool to 25°C. The reaction mixture was transferred to a rotary evaporator with gentle heating at between 50 and 55°C. After 1 hour, when most of the volatiles had been removed, the reaction mixture was added to methanol (each 25 milliliters of solution was added to 0.75 liter of methanol) to precipitate the polymer using a Waring blender. The precipitated polymer was collected by filtration, washed with methanol, and air-dried to yield 13 grams of off-white powder. The polymer had about 1.0 CH_2Cl groups per every 4 repeat units. A solution was then prepared containing 11 grams of the chloromethylated polymer in 100 milliliters (87.4 grams) of N,N-dimethylacetamide and the solution was magnetically stirred at 25°C with sodium acrylate (30 grams) for 1 week. The reaction mixture was then filtered and added to methanol using a Waring blender in relative amounts of 25 milliliters of polymer solution per 0.75 liter of methanol. The white powder that precipitated was reprecipitated into methanol from a 20 weight percent solids solution in methylene chloride and was them air dried to yield 7.73 grams of a white powder. The polymer had 1 acrylate group for every 8 repeat units, and 1 chloromethyl group for every 8 repeat units.

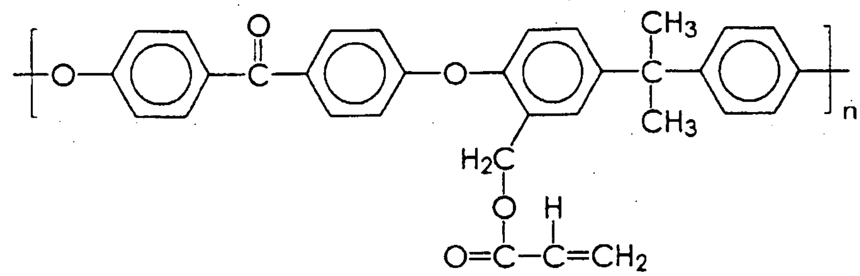
50 parts by weight of the first polymer were admixed with 50 parts by weight of the second polymer to result in a mixture containing equal parts by weight of both polymers. A solution was prepared containing 40 percent by weight solids of the polymer mixture in *N*-methylpyrrolidone. Thereafter, a sensitizer (Michler's ketone) was added to the solution in an amount of about 0.75 percent by weight of the solution and more solvent was added, bringing the solution to a solids content of 37 percent by weight. The resulting blend had a weight average molecular weight of about 34,000 and a degree of acryloylation of about 0.78 milliequivalents of acryloyl groups per gram of resin.

The solution thus formed was coated onto spinning silane-treated silicon wafers and the coated wafers were heated at 70°C for 5 minutes. The wafers were then allowed to cool to 25°C, followed by covering the wafers with masks and exposure to ultraviolet light at a wavelength of 365 nanometers, amounting to 2,500 milliJoules/cm^2. The exposed films were then heated to 70°C for 5 minutes post exposure bake, followed by cooling to 25°C. The films were developed with 60:40 chloroform/cyclohexanone developer, washed with 90:10 hexanes/cyclohexanone, and then dried at 70°C. The processed wafers were transferred to an oven at 25°C, and the oven temperature was raised at 2°C per minute

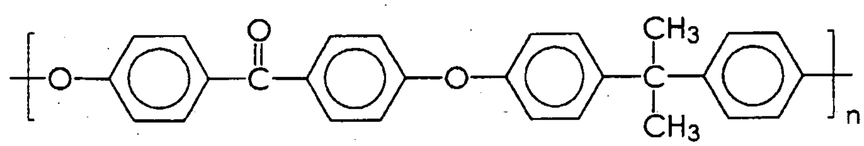
to 260°C to effect post-cure. During post-cure, heat stable, solvent resistant sites were formed. The post-cured, crosslinked polymers were heat stable, chemically inert to thermal ink jet inks (including a black ink available from Canon K.K. with a pH of 9.6 after exposure to the ink for 5 weeks at 65°C), electrically insulating, and mechanically robust, and exhibited low shrinkage during post-cure. Clean features were developed at resolutions of 300 and 600 dots per inch.

EXAMPLE II

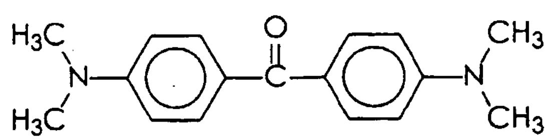
An acryloylated poly(4-CPK-BPA) with a weight average molecular weight of about 60,000 and having 1 acryloyl group per repeat unit and 1 chloromethyl group per repeat unit (7 grams), prepared as described in Example I, of the structure



and a poly(4-CPK-BPA) with a weight average molecular weight of 5,600 (3 grams), prepared in a manner similar to that described for the preparation of poly(4-CPK-BPA) of M_w 5,875 in Example I except that heating at 175°C was for 30 hours instead of 48 hours, of the structure

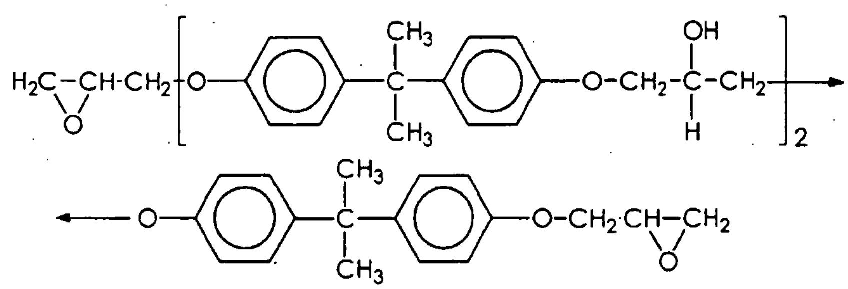


were combined and diluted to 37 weight percent solids with N-methylpyrrolidinone (15 grams). Michler's ketone of the formula



was added in an amount of from about 0.3 to about 0.5 percent by weight of the resin solids before exposure to develop 30 micron thick films. The resulting blend had a weight average molecular weight of about 44,000 and a degree of acryloylation of about 1.31 milliequivalents of acryloyl groups per gram of resin. A heater wafer with a phosphosilicate glass layer was spin coated with a solution of Z6020 adhesion promoter (0.01 weight percent in methanol {95 parts} and water {5 parts}, available from Dow Corning) at 3000 revolutions per minute for 10 seconds and dried at 100°C for between 2 and 10 minutes. The wafer was then allowed to cool at 25°C over 5 minutes before spin coating the polyarylene ether ketone blended photoresist solution onto the wafer at between 1000 and 3000 revolutions per minute for between 30 and 60 seconds. The film was heated (soft baked) in an oven for between 10 and 15 minutes at 70°C. After cooling to 25°C over 5 minutes, the film was covered with a mask and exposed to 365 nanometer ultraviolet light, amounting to between 150 and 1500 milliJoules per cm^2. The exposed wafer was then heated at 70°C for 2 minutes post exposure bake, followed by cooling to 25°C over 5 minutes. The film was developed with 6:4 chloroform/cyclohexanone developer, washed with 9:1 hexanes/cyclohexanone and then dried at 70°C for 2 minutes. A second developer/wash cycle was carried out if necessary to obtain a wafer with clean features. The processed wafer was transferred to an oven at 25°C, and the oven temperature was raised from 25 to 90°C at 2°C per minute. The temperature was

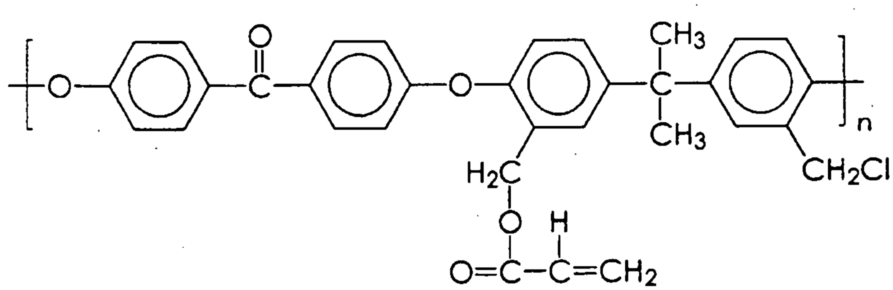
maintained at 90°C for 2 hours, and then increased to 260°C at 2°C per minute. The oven temperature was maintained at 260°C for 2 hours and then the oven was turned off and the temperature was allowed to gradually cool to 25°C. When thermal cure of the photoresist films was carried out under inert atmosphere such as argon or nitrogen, there was markedly reduced oxidation of the developed film and improved thermal and hydrolytic stability of the resultant devices. Moreover, adhesion was improved to the underlying substrate. If desired, the heat cure of the first developed layer can be stopped between 80 and 260°C before the second layer is spin coated on top. A second thicker layer was deposited by repeating the above procedure a second time. This process is intended to be a guide in that procedures can be outside the specified conditions depending on film thickness and photoresist molecular weight. Films at 30 microns were developed with clean features at 600 dots per inch. The photopatternable polymer blend solution was further admixed with epoxy resin in relative amounts of about 90 parts by weight polymer and about 10 parts by weight epoxy resin, EPON 1001F, available from Shell Chemical Company, Houston, Texas, believed to be of the formula



"Y" curative (meta-phenylene diamine) was used to cure the epoxy resin at 10 weight percent addition of curative per gram of epoxy resin solids. The same spin conditions, soft bake, photoexposure, and development conditions were used in the case of the epoxy blend as in that without the epoxy resin material. Incorporation of the epoxy resin into the photopatternable polymer material improved the adhesion of the photopatternable layer to the heater plate. Subsequent to imaging and during cure of the photopatternable polymer, the epoxy reacted with the heater layer to form strong chemical bonds with that layer, improving adhesive strength and solvent resistance of the interface. The presence of the epoxy may also improve the hydrophilicity of the photopatternable polymer and thus may improve the wetting properties of the layer, thereby improving the refill characteristics of the printhead. Thermal ink jet printhead devices were made with the above composition which resisted sulfolane based ink jet compositions and alkaline inks of pH 8 which contained N-cyclohexylpyrrolidinone and imidazole.

EXAMPLE III

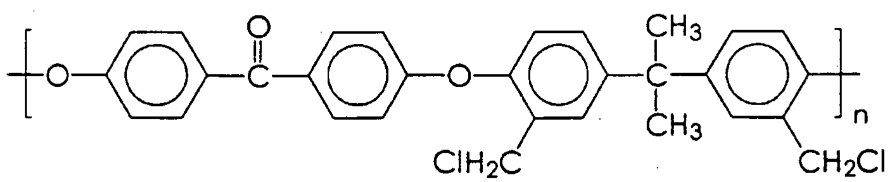
An acryloylated poly(4-CPK-BPA) with a weight average molecular weight of about 25,000 and having 0.75 acryloyl group and 0.75 chloromethyl group per repeat unit of the structure



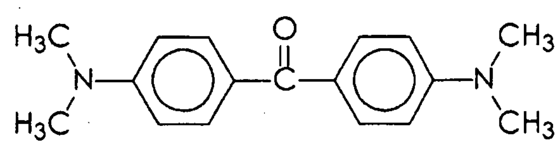
was prepared as follows. A 1 liter, 3-neck round-bottom flask equipped with a Dean-Stark (Barrett) trap, condenser, mechanical stirrer, argon inlet, and stopper was situated in a silicone oil bath. 4,4'-Dichlorobenzophenone (Aldrich 11,370, Aldrich Chemical Co., Milwaukee, WI, 53.90 grams), bis-phenol A (Aldrich 23,965-8, 45.42 grams), potassium carbonate (65.56 grams), anhydrous *N,N*-dimethylacetamide (300 milliliters), and toluene (55 milliliters) were added to the flask and heated to 175°C (oil bath temperature) while the volatile toluene component was collected and removed. After 24 hours of heating at 175°C with continuous stirring, the reaction mixture was filtered to remove potassium carbonate and precipitated into methanol (2 gallons). The polymer (poly(4-CPK-BPA)) was isolated in 86% yield after

filtration and drying *in vacuo*. As a result of the stoichiometries used in the reaction, it is believed that this polymer had end groups derived from 4,4-dichlorobenzophenone. Gel permeation chromatography (gpc) (elution solvent was tetrahydrofuran) analysis was as follows: M_n 4,334, M_{peak} 10,214, M_w 11,068, M_z 10,214, and M_{z+1} 28,915. Solution cast films from methylene chloride were clear, tough, and flexible. The polymer thus prepared was chloromethylated as follows. A solution of chloromethyl ether in methyl acetate was made by adding 282.68 grams (256 milliliters) of acetyl chloride to a mixture of dimethoxy methane (313.6 grams, 366.8 milliliters) and methanol (10 milliliters) in a 5 liter 3-neck round-bottom flask equipped with a mechanical stirrer, argon inlet, reflux condenser, and addition funnel. The solution was diluted with 1,066.8 milliliters of 1,1,2,2-tetrachloroethane and then tin tetrachloride (2.4 milliliters) was added via a gas-tight syringe along with 1,1,2,2-tetrachloroethane (133.2 milliliters) using an addition funnel. The reaction solution was heated to 500°C. Thereafter, a solution of the poly(4-CPK-BPA) (160.8 grams) in 1,000 milliliters of tetrachloroethane was added rapidly. The reaction mixture was then heated to reflux with an oil bath set at 110°C. After 4 hours reflux with continuous stirring, heating was discontinued and the mixture was allowed to cool to 25°C. The reaction mixture was transferred in stages to a 2 liter round bottom flask and concentrated using a rotary evaporator with gentle heating up to 50°C while reduced pressure was maintained with a vacuum pump trapped with liquid nitrogen. The concentrate was added to methanol (4 gallons) to precipitate the polymer using a Waring blender. The polymer was isolated by filtration and vacuum dried to yield 200 grams of poly(4-CPK-BPA) with 1.5 chloromethyl groups per repeat unit as identified using ^{1}H NMR spectroscopy. Solvent free polymer was obtained by reprecipitation of the polymer (75 grams) in methylene chloride (500 grams) into methanol (3 gallons) followed by filtration and vacuum drying. Gel permeation chromatography (gpc) (elution solvent was tetrahydrofuran) analysis was as follows: M_n 5,580, M_{peak} 15,242, M_w 17,169, M_z 36,837, and M_{z+1} 57,851. The chloromethylated polymer was then acryloylated as follows. A solution was prepared containing 90 grams of the chloromethylated polymer with 2 chloromethyl groups per repeat unit in 639 milliliters (558.5 grams) of *N,N*-dimethylacetamide and the solution was magnetically stirred at 25°C with sodium acrylate (51.39 grams) for 1 week. The reaction mixture was then centrifuged, and the supernate was added to methanol (4.8 gallons) using a Waring blender in relative amounts of 25 milliliters of polymer solution per 0.75 liter of methanol. The white powder that precipitated was filtered, and the wet filter cake was washed with water (3 gallons) and then methanol (3 gallons). The polymer was then isolated by filtration and vacuum dried to yield a white powder. The polymer had 0.75 acrylate group for every repeating monomer unit and 0.75 chloromethyl group for every repeating monomer unit. Gel permeation chromatography (gpc) (elution solvent was tetrahydrofuran) analysis was as follows: M_n 7,000, M_{peak} 17,376, M_w 22,295, M_z 50,303, and M_{z+1} 80,995.

A poly(4-CPK-BPA) with a weight average molecular weight of 11,000 and having 2 chloromethyl groups per repeat unit, of the structure

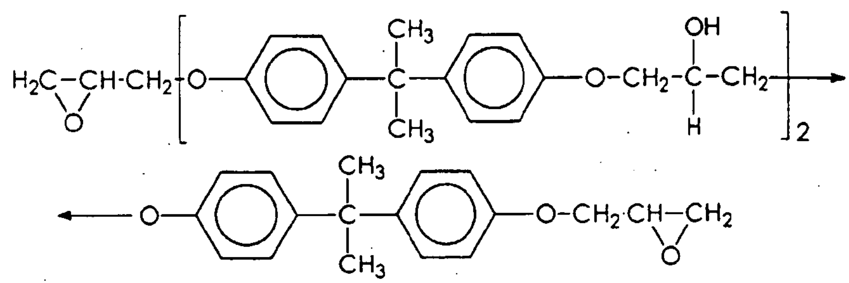


was prepared as described in Example I. Thereafter, 7 grams of the acryloylated and chloromethylated polymer with weight average molecular weight of about 25,000 and 3 grams of the chloromethylated polymer with weight average molecular weight of about 11,000 were combined and diluted to 37 weight percent solids with N-methylpyrrolidinone (15 grams). Michler's ketone of the formula



was added in an amount of from about 0.3 to about 0.5 percent by weight of the resin solids before exposure to develop 30 micron thick films. The blend had a weight average molecular weight of about 20,800 and a degree of acryloylation of about 1.05 milliequivalents per gram. A heater wafer with a phosphosilicate glass layer was spin coated with a solution of Z6020 adhesion promoter (0.01 weight percent in methanol {95 parts} and water {5 parts}, available from Dow Corning) at 3000 revolutions per minute for 10 seconds and dried at 100°C for between 2 and 10 minutes. The wafer was then allowed to cool at 25°C over 5 minutes before spin coating the polyarylene ether ketone blended

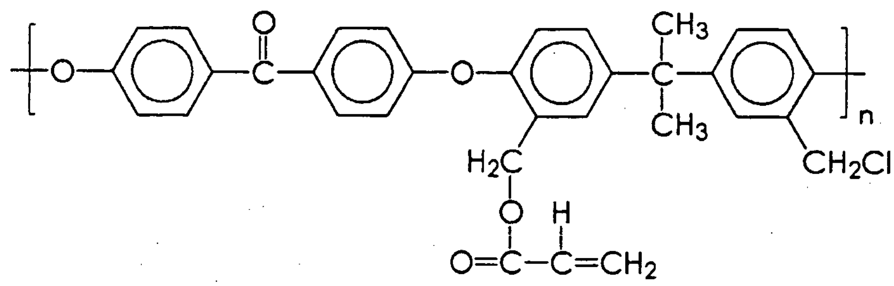
photoresist solution onto the wafer at between 1000 and 3000 revolutions per minute for between 30 and 60 seconds. The film was heated (soft baked) in an oven for between 10 and 15 minutes at 70°C. After cooling to 25°C over 5 minutes, the film was covered with a mask and exposed to 365 nanometer ultraviolet light, amounting to between 150 and 1500 milliJoules per cm^2. The exposed wafer was then heated at 70°C for 2 minutes post exposure bake, followed by cooling to 25°C over 5 minutes. The film was developed with 6:4 chloroform/cyclohexanone developer, washed with 9:1 hexanes/cyclohexanone and then dried at 70°C for 2 minutes. A second developer/wash cycle was carried out if necessary to obtain a wafer with clean features. The processed wafer was transferred to an oven at 25°C, and the oven temperature was raised from 25 to 90°C at 2°C per minute. The temperature was maintained at 90°C for 2 hours, and then increased to 260°C at 2°C per minute. The oven temperature was maintained at 260°C for 2 hours and then the oven was turned off and the temperature was allowed to gradually cool to 25°C. When thermal cure of the photoresist films was carried out under inert atmosphere such as argon or nitrogen, there was markedly reduced oxidation of the developed film and improved thermal and hydrolytic stability of the resultant devices. Moreover, adhesion was improved to the underlying substrate. If desired, the heat cure of the first developed layer can be stopped between 80 and 260°C before the second layer is spin coated on top. A second thicker layer was deposited by repeating the above procedure a second time. This process is intended to be a guide in that procedures can be outside the specified conditions depending on film thickness and photoresist molecular weight. Films at 30 microns were developed with clean features at 600 dots per inch. The photopatternable polymer blend solution was further admixed with epoxy resin in relative amounts of about 90 parts by weight polymer and about 10 parts by weight epoxy resin, EPON 1001F, available from Shell Chemical Company, Houston, Texas, believed to be of the formula



"Y" curative (meta-phenylene diamine) was used to cure the epoxy resin at 10 weight percent addition of curative per gram of epoxy resin solids. The same spin conditions, soft bake, photoexposure, and development conditions were used in the case of the epoxy blend as in that without the epoxy resin material. Incorporation of the epoxy resin into the photopatternable polymer material improved the adhesion of the photopatternable layer to the heater plate. Subsequent to imaging and during cure of the photopatternable polymer, the epoxy reacted with the heater layer to form strong chemical bonds with that layer, improving adhesive strength and solvent resistance of the interface. The presence of the epoxy may also improve the hydrophilicity of the photopatternable polymer and thus may improve the wetting properties of the layer, thereby improving the refill characteristics of the printhead. Thermal ink jet printhead devices were made with the above composition which resisted sulfolane based ink jet compositions and alkaline inks of pH 8 which contained N-cyclohexylpyrrolidinone and imidazole.

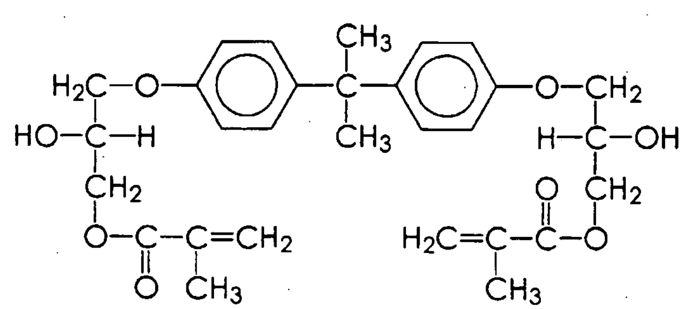
EXAMPLE IV

Acryloylated poly(4-CPK-BPA) with a weight average molecular weight of 60,000 and having 0.75 acryloyl group and 0.75 chloromethyl group per repeat unit, of the general structure



is prepared as follows. A 1 liter, 3-neck round-bottom flask equipped with a Dean-Stark (Barrett) trap, condenser, mechanical stirrer, argon inlet, and stopper is situated in a silicone oil bath. 4,4'-Dichlorobenzophenone (Aldrich 11,370, Aldrich Chemical Co., Milwaukee, WI, 50 grams), bis-phenol A (Aldrich 23,965-8, 48.96 grams), potassium carbonate (65.56 grams), anhydrous *N,N*-dimethylacetamide (300 milliliters), and toluene (55 milliliters) are added to the flask and heated to 175°C (oil bath temperature) while the volatile toluene component is collected and removed. After 24 hours of heating at 175°C with continuous stirring, it is believed that the reaction product precipitated into methanol, if analyzed by gel permeation chromatography (gpc) (elution solvent is tetrahydrofuran), will have approximately the following results: M_n 3100, M_w 6250. As a result of the stoichiometries used in the reaction, it is believed that this polymer will have end groups derived from bis-phenol A. This polymer contains 7 mol% N,N-dimethylacetamide as residual solvent. When the residual N,N-dimethylacetamide exceeds 5 mol% of the polymer, the chloromethylation reaction of the next step proceeds only to a maximum value of 1 chloromethyl group per every 4 monomer repeat units. A solution of chloromethyl ether in methyl acetate is made by adding 35.3 grams of acetyl chloride to a mixture of dimethoxy methane (45 milliliters) and methanol (1.25 milliliters) in a 500 milliliter 3-neck round-bottom flask equipped with a mechanical stirrer, argon inlet, reflux condenser, and addition funnel. The solution is diluted with 150 milliliters of 1,1,2,2-tetrachloroethane and then tin tetrachloride (0.3 milliliters) is added via syringe. The solution is heated to reflux with an oil bath set at 110°C. Thereafter, a solution of the poly(4-CPK-BPA) containing residual solvent (10 grams of polymer) in 125 milliliters of 1,1,2,2-tetrachloroethane is added over 8 minutes. After two hours reflux with continuous stirring, heating is discontinued and the mixture is allowed to cool to 25°C. The reaction mixture is transferred to a rotary evaporator with gentle heating at between 50 and 55°C. After 1 hour, when most of the volatiles have been removed, the reaction mixture is added to methanol (each 25 milliliters of solution is added to 0.75 liter of methanol) to precipitate the polymer using a Waring blender. The precipitated polymer is collected by filtration, washed with methanol, and air-dried to yield off-white powder. It is believed that the polymer will have about 1 CH_2Cl group per every 4 repeat units. A solution is then prepared containing 11 grams of the chloromethylated polymer in 100 milliliters (87.4 grams) of N,N-dimethylacetamide and the solution is magnetically stirred at 25°C with sodium acrylate (30 grams) for 1 week. The reaction mixture is then filtered and added to methanol using a Waring blender in relative amounts of 25 milliliters of polymer solution per 0.75 liter of methanol. The white powder that precipitates is reprecipitated into methanol from a 20 weight percent solids solution in methylene chloride and is then air dried to yield a white powder. It is believed that the polymer will have 1 acrylate group for every 8 repeat units, and 1 chloromethyl group for every 8 repeat units.

Bisphenol A bispropylene glycol dimethacrylate, molecular weight 512, is prepared as disclosed in, for example, "Bis-Methacryloxy Bisphenol-A Epoxy Networks: Synthesis, Characterization, Thermal and Mechanical Properties," A. Banthia et al., *Polymer Preprints*, ***22***(1), 209 (1981),

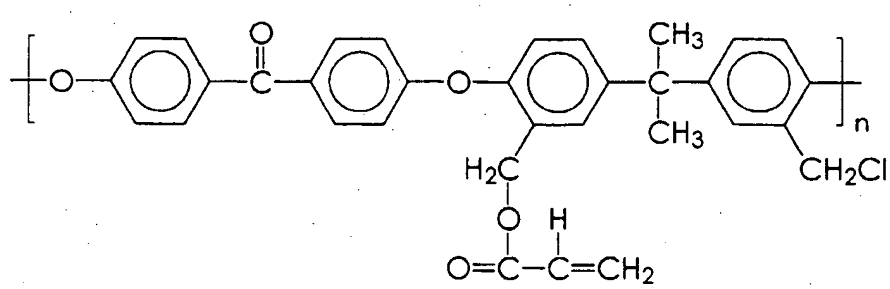


The acryloylated and chloromethylated polymer (8 grams) and the bisphenol A bispropylene glycol dimethacrylate are

combined and diluted to 37 weight percent solids with N-methylpyrrolidinone (15 grams). The resulting blend has a weight average molecular weight of about 20,000 and a degree of acryloylation of about 1.27 milliequivalents of acryloyl groups per gram of blend. Michler's ketone is added in an amount of from about 0.3 to about 0.5 percent by weight of the resin solids before exposure to develop 30 micron thick films. A heater wafer with a phosphosilicate glass layer is spin coated with a solution of Z6020 adhesion promoter (0.01 weight percent in methanol {95 parts} and water {5 parts}, available from Dow Corning) at 3000 revolutions per minute for 10 seconds and dried at 100°C for between 2 and 10 minutes. The wafer is then allowed to cool at 25°C over 5 minutes before spin coating the polyarylene ether ketone blended photoresist solution onto the wafer at between 1000 and 3000 revolutions per minute for between 30 and 60 seconds. The film is heated (soft baked) in an oven for between 10 and 15 minutes at 70°C. After cooling to 25°C over 5 minutes, the film is covered with a mask and exposed to 365 nanometer ultraviolet light, amounting to between 150 and 1500 milliJoules per cm^2. The exposed wafer is then heated at 70°C for 2 minutes post exposure bake, followed by cooling to 25°C over 5 minutes. The film is developed with 6:4 chloroform/cyclohexanone developer, washed with 9:1 hexanes/cyclohexanone and then dried at 70°C for 2 minutes. A second developer/wash cycle is carried out if necessary to obtain a wafer with clean features. The processed wafer is transferred to an oven at 25°C, and the oven temperature is raised from 25 to 90°C at 2°C per minute. The temperature is maintained at 90°C for 2 hours, and then increased to 260°C at 2°C per minute. The oven temperature is maintained at 260°C for 2 hours and then the oven is turned off and the temperature is allowed to cool gradually to 25°C. When thermal cure of the photoresist films is carried out under inert atmosphere such as argon or nitrogen, there is markedly reduced oxidation of the developed film and improved thermal and hydrolytic stability of the resultant devices. Moreover, adhesion is improved to the underlying substrate. If desired, the heat cure of the first developed layer can be stopped between 80 and 260°C before the second layer is spin coated on top. A second thicker layer is deposited by repeating the above procedure a second time. This process is intended to be a guide in that procedures can be outside the specified conditions depending on film thickness and photoresist molecular weight. Films at 30 microns can be developed with clean features at 600 dots per inch.

EXAMPLE V

Acryloylated poly(4-CPK-BPA) with a weight average molecular weight of 25,000 and having 0.75 acryloyl group and 0.75 chloromethyl group per repeat unit (80 parts by weight), of the structure



prepared as described in Example III, and polymethyl methacrylate having a weight average molecular weight of 15,000 (obtained from Sigma Chemical Co., St. Louis, MO) (20 parts by weight) are combined and diluted to 37 weight percent solids with N-methylpyrrolidinone (150 grams). The resulting blend had a weight average molecular weight of about 23,000 and a degree of acrylolylation of about 1.20 milliequivalents per gram. Michler's ketone is added in an amount of about 1.5 percent by weight of the resin solids before exposure to develop 30 micron thick films. A heater wafer with a phosphosilicate glass layer is spin coated with a solution of Z6020 adhesion promoter (0.01 weight percent in methanol {95 parts} and water {5 parts}, available from Dow Corning) at 3000 revolutions per minute for 10 seconds and dried at 100°C for between 2 and 10 minutes. The wafer is then allowed to cool at 25°C over 5 minutes before spin coating the polyarylene ether ketone blended photoresist solution onto the wafer at between 1000 and 3000 revolutions per minute for between 30 and 60 seconds. The film is heated (soft baked) in an oven for between 10 and 15 minutes at 70°C. After cooling to 25°C over 5 minutes, the film is covered with a mask and exposed to 365 nanometer ultraviolet light, amounting to between 150 and 1500 milliJoules per cm^2. The exposed wafer is then heated at 70°C for 2 minutes post exposure bake, followed by cooling to 25°C over 5 minutes. The film is developed with 6:4 chloroform/cyclohexanone developer, washed with 9:1 hexanes/cyclohexanone and then dried at 70°C for 2 minutes. A second developer/wash cycle is carried out if necessary to obtain a wafer with clean features. The processed wafer is transferred to an oven at 25°C, and the oven temperature is raised from 25 to 90°C at 2°C per minute. The temperature is maintained at 90°C for 2 hours, and then increased to 260°C at 2°C per minute. The oven temperature is maintained at 260°C for

2 hours and then the oven is turned off and the temperature is allowed to cool gradually to 25°C. When thermal cure of the photoresist films is carried out under inert atmosphere such as argon or nitrogen, it is believed that there will be markedly reduced oxidation of the developed film and improved thermal and hydrolytic stability of the resultant devices. Moreover, it is believed that adhesion will be improved to the underlying substrate. If desired, the heat cure of the first developed layer can be stopped between 80 and 260°C before the second layer is spin coated on top. A second thicker layer is deposited by repeating the above procedure a second time. This process is intended to be a guide in that procedures can be outside the specified conditions depending on film thickness and photoresist molecular weight. It is believed that films at 30 microns can be developed with clean features at 600 dots per inch.

EXAMPLE VI

(a) A solution of chloromethyl ether in methyl acetate was made by adding 282.68 grams (256 milliliters) of acetyl chloride to a mixture of dimethoxy methane (313.6 grams, 366.8 milliliters) and methanol (10 milliliters) in a 5 liter 3-neck round-bottom flask equipped with a mechanical stirrer, argon inlet, reflux condenser, and addition funnel. The solution was diluted with 1,066.8 milliliters of 1,1,2,2-tetrachloroethane and then tin tetrachloride (2.4 milliliters) was added via a gas-tight syringe along with 1,1,2,2-tetrachloroethane (133.2 milliliters) using an addition funnel. The reaction solution was heated to 500°C. Thereafter, a solution of poly(4-CPK-BPA) prepared as described in Example VIII (160.8 grams) in 1,000 milliliters of tetrachloroethane was added rapidly. The reaction mixture was then heated to reflux with an oil bath set at 110°C. After four hours reflux with continuous stirring, heating was discontinued and the mixture was allowed to cool to 25°C. The reaction mixture was transferred in stages to a 2 liter round bottom flask and concentrated using a rotary evaporator with gentle heating up to 50°C while reduced pressure was maintained with a vacuum pump trapped with liquid nitrogen. The concentrate was added to methanol (4 gallons) to precipitate the polymer using a Waring blender. The polymer was isolated by filtration and vacuum dried to yield 200 grams of poly (4-CPK-BPA) with 1.5 chloromethyl groups per repeat unit as identified using ^{1}H NMR spectroscopy. When the same reaction was carried out for 1, 2, 3, and 4 hours, the amount of chloromethyl groups per repeat unit was 0.76, 1.09, 1.294, and 1.496, respectively.

Solvent free polymer was obtained by reprecipitation of the polymer (75 grams) in methylene chloride (500 grams) into methanol (3 gallons) followed by filtration and vacuum drying to yield 70.5 grams (99.6% theoretical yield) of solvent free polymer.

When the reaction was carried out under similar conditions except that 80.4 grams of poly(4-CPK-BPA) was used instead of 160.8 grams and the amounts of the other reagents were the same as indicated above, the polymer is formed with 1.31, 1.50, 1.75, and 2 chloromethyl groups per repeat unit in 1, 2, 3, and 4 hours, respectively, at 110°C (oil bath temperature).

When 241.2 grams of poly(4-CPK-BPA) was used instead of 160.8 grams with the other reagents fixed, poly(CPK-BPA) was formed with 0.79, 0. 90, 0.98, 1.06, 1.22, and 1.38 chloromethyl groups per repeat unit in 1, 2, 3, 4, 5, and 6 hours, respectively, at 110°C (oil bath temperature).

When 321.6 grams of poly(4-CPK-BPA) was used instead of 160.8 grams with the other reagents fixed, poly(CPK-BPA) was formed with 0.53, 0.59, 0.64, 0.67, 0.77, 0.86, 0.90, and 0.97 chloromethyl groups per repeat unit in 1, 2, 3, 4, 5, 6, 7, and 8 hours, respectively, at 110°C (oil bath temperature).

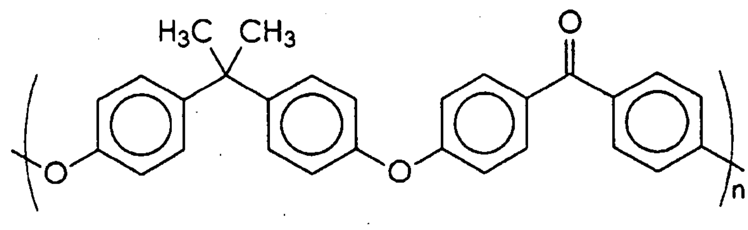
(b) A solution was prepared containing 90 grams of a chloromethylated polymer prepared as described in (a) above with 1.5 chloromethyl groups per repeat unit in 639 milliliters (558.5 grams) of *N,N*-dimethylacetamide and the solution was magnetically stirred at 25°C with sodium acrylate (51.39 grams) for 1 week. The reaction mixture was then centrifuged, and the supernate was added to methanol (4.8 gallons) using a Waring blender in relative amounts of 25 milliliters of polymer solution per 0.75 liter of methanol. The white powder that precipitated was filtered, and the wet filter cake was washed with water (3 gallons) and then methanol (3 gallons). The polymer was then isolated by filtration and vacuum dried to yield 73.3 grams of a white powder. The polymer had 3 acrylate groups for every 4 repeating monomer units and 3 chloromethyl groups for every 4 repeating monomer units and a weight average molecular weight of about 25,000.

When the reaction was repeated with poly(4-CPK-BPA) with 2 chloromethyl groups per repeat unit and the other reagents remained the same, the reaction took four days to achieve 0.76 acrylate groups per repeat unit and 1.24 chloromethyl groups per repeat unit.

When the reaction was repeated with poly(4-CPK-BPA) with 1.0 chloromethyl groups per repeat unit and the other reagents remained the same, the reaction took 14-days to achieve 0.75 acrylate groups per repeat unit and 2.5 chloromethyl groups per repeat unit.

EXAMPLE VII

A polyarylene ether ketone of the formula

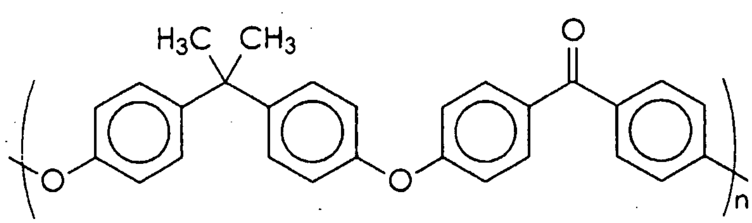


was prepared as described in Example VII. A solution of chloromethyl ether in methyl acetate was made by adding 35.3 grams of acetyl chloride to a mixture of dimethoxy methane (45 milliliters) and methanol (1.25 milliliters) in a 500 milliliter 3-neck round-bottom flask equipped with a mechanical stirrer, argon inlet, reflux condenser, and addition funnel. The solution was diluted with 150 milliliters of 1,1,2,2-tetrachloroethane and then tin tetrachloride (0.3 milliliters) was added via syringe. The solution was heated to reflux with an oil bath set at 110°C. Thereafter, a solution of poly(4-CPK-BPA) (10 grams) in 125 milliliters of 1,1,2,2-tetrachloroethane was added over 8 minutes. After two hours reflux with continuous stirring, heating was discontinued and the mixture was allowed to cool to 25°C. The reaction mixture was transferred to a rotary evaporator with gentle heating at between 50 and 55°C. After 1 hour, when most of the volatiles had been removed, the reaction mixture was added to methanol (each 25 milliliters of solution was added to 0.75 liter of methanol) to precipitate the polymer using a Waring blender. The precipitated polymer was collected by filtration, washed with methanol, and air-dried to yield 13 grams of off-white powder. The polymer had about 1.5 CH_2Cl groups per repeat unit.

A chloromethylated polyarylene ether ketone was prepared as described in (a) above. A solution was then prepared containing 11 grams of the chloromethylated polymer in 100 milliliters (87.4 grams) of N,N-dimethylacetamide and the solution was magnetically stirred at 25°C with sodium acrylate (30 grams) for 1 week. The reaction mixture was then filtered and added to methanol using a Waring blender in relative amounts of 25 milliliters of polymer solution per 0.75 liter of methanol. The white powder that precipitated was reprecipitated into methanol from a 20 weight percent solids solution in methylene chloride and was them air dried to yield 7.73 grams of a white powder. The polymer had 3 acrylate groups for every 4 repeating monomer units and 3 chloromethyl groups for every 4 repeating monomer units.

EXAMPLE VIII

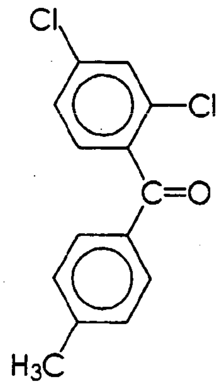
(a) A polymer of the formula



wherein n represents the number of repeating monomer units was prepared as follows. A 1-liter, 3-neck round-bottom flask equipped with a Dean-Stark (Barrett) trap, condenser, mechanical stirrer, argon inlet, and stopper was situated in a silicone oil bath. 4,4'-Difluorobenzophenone (Aldrich Chemical Co., Milwaukee, WI, 16.59 grams), bisphenol A (Aldrich 14.18 grams, 0.065 mol), potassium carbonate (21.6 grams), anhydrous *N,N*-dimethylacetamide (100 milliliters), and toluene (30 milliliters) were added to the flask and heated to 175°C (oil bath temperature) while the volatile toluene component was collected and removed. After 4 hours of heating at 175°C with continuous stirring, the reaction mixture was allowed to cool to 25°C. The solidified mass was treated with acetic acid (vinegar) and extracted with methylene chloride, filtered, and added to methanol to precipitate the polymer, which was collected by filtration, washed with water, and then washed with methanol. The yield of vacuum dried product, poly(4-FPK-BPA), was 12.22 grams. The polymer was analyzed by gel permeation chromatography (gpc) (elution solvent was tetrahydrofuran) with the following results: M_n 5,158, M_{peak} 15,080, M_w 17,260, and M_{z+1} 39,287. To obtain a lower molecular weight, the reaction can be repeated with a 15 mol% offset in stoichiometry. (b) The polymer as prepared in (a) above is treated as described in Example VI(b).

EXAMPLE IX

(a) 4'-Methylbenzoyl-2,4-dichlorobenzene, of the formula

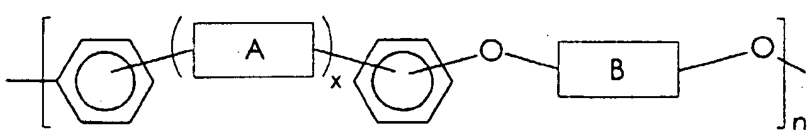


was prepared as follows. To a 2-liter flask equipped with a mechanical stirrer, argon inlet, Dean Stark trap, condenser, and stopper and situated in an oil bath was added toluene (152 grams). The oil bath temperature was raised to 130°C and 12.5 grams of toluene were removed. There was no indication of water. The flask was removed from the oil bath and allowed to cool to 25°C. 2,4-Dichlorobenzoyl chloride (0.683 mol, 143 grams) was added to form a solution. Thereafter, anhydrous aluminum chloride (0.8175 mol, 109 grams) was added portion-wise over 15 minutes with vigorous gas evolution of hydrochloric acid as determined by odor. The solution turned orange-yellow and then red. The reaction was stirred for 16 hours under argon, and on removing the solvent, a solid lump was obtained. The mass was extracted with methylene chloride (1 liter), which was then dried over potassium carbonate and filtered. The filtrate was concentrated using a rotary evaporator and a vacuum pump to yield an oil which, upon cooling, became a solid crystalline mass. Recrystallization from methanol (1 liter) at -15°C gave 82.3 grams of 4'-methylbenzoyl-2,4-dichlorobenzene (melting point 55-56°C) in the first crop, 32 grams of product (from 500 milliliters of methanol) in the second crop, and 16.2 grams of product in the third crop. The total recovered product was 134.7 grams in 65.6% yield.

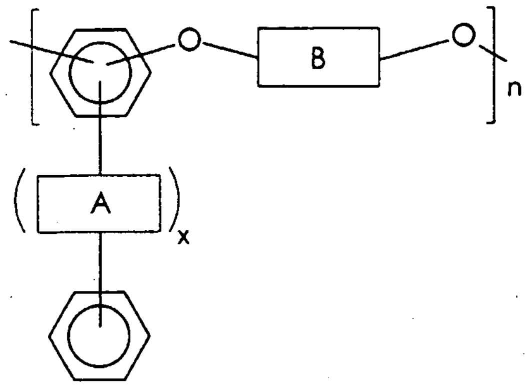
(b) The polymer as described in (b) above is treated as described in Example VI(b).

Claims

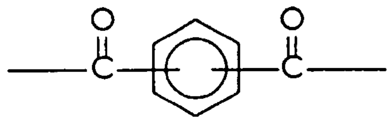
1. A composition which comprises a mixture of (A) a first component comprising a polymer, at least some of the monomer repeat units of which have at least one photosensitivity-imparting group thereon, said polymer having a first degree of photosensitivity-imparting group substitution measured in milliequivalents of photosensitivity-imparting group per gram and being of the general formula



or



wherein x is an integer of 0 or 1, A is



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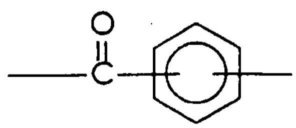

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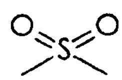

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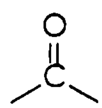

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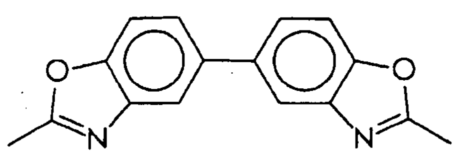

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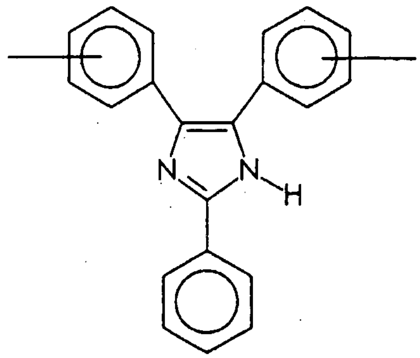
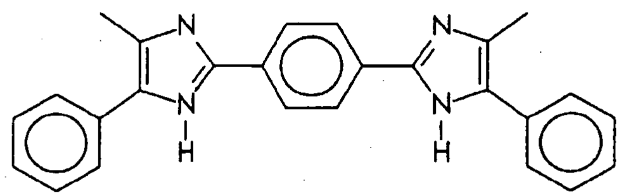
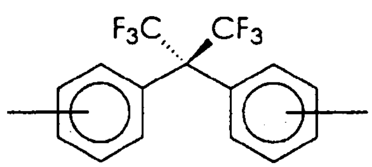


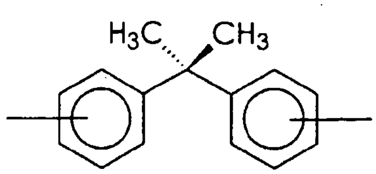


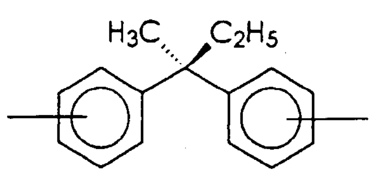
-O-,

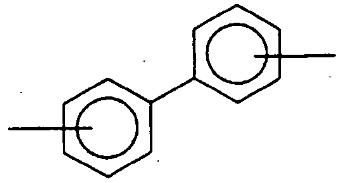
$-C(CH_3)_2-$,

or mixtures thereof, B is





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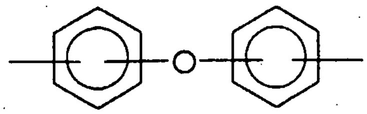
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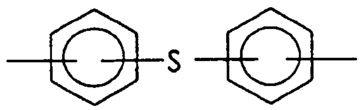
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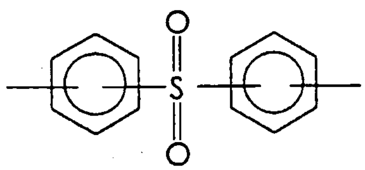
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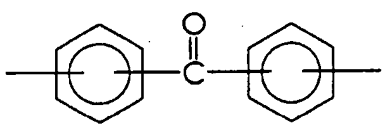
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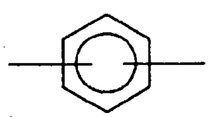
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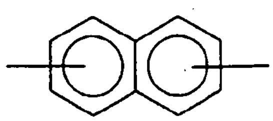
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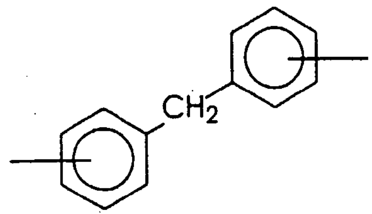

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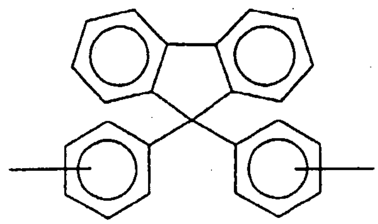

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$$-\left(CH_2\right)_v-$$

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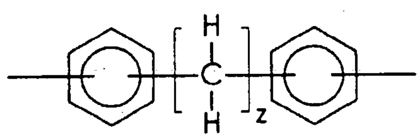
wherein v is an integer of from 1 to about 20,



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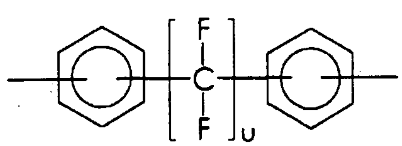
wherein z is an integer of from 2 to about 20,



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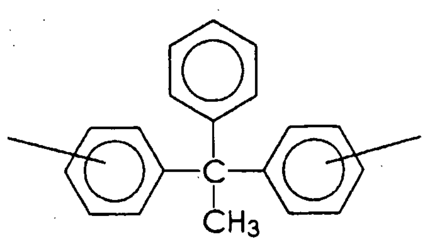
wherein u is an integer of from 1 to about 20,



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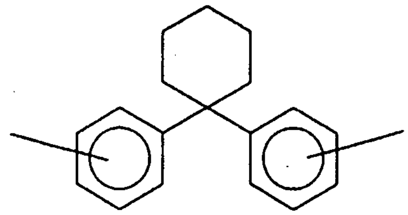

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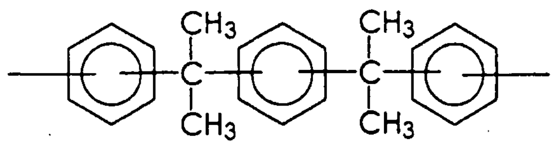

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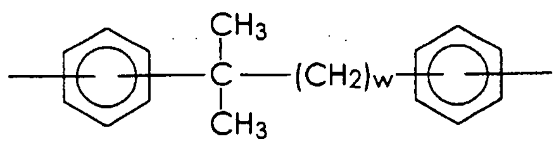

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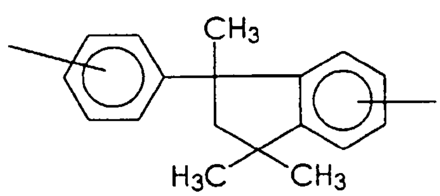
wherein w is an integer of from 1 to about 20,



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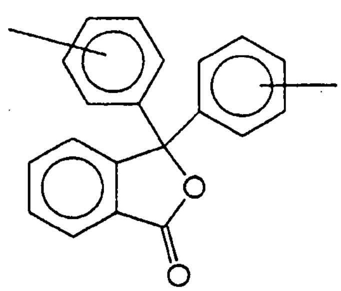

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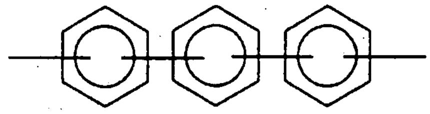

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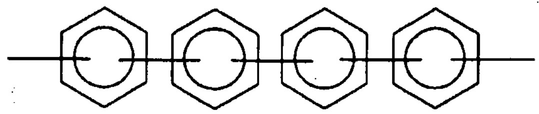

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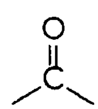
or mixtures thereof, and n is an integer representing the number of repeating monomer units, and (B) a second component which comprises either (1) a polymer having a second degree of photosensitivity-imparting group substitution measured in milliequivalents of photosensitivity-imparting group per gram lower than the first degree of photosensitivity-imparting group substitution, wherein said second degree of photosensitivity-imparting group substitution may be zero, wherein the mixture of the first component and the second component has a third degree of photosensitivity-imparting group substitution measured in milliequivalents of photosensitivity-imparting group per gram which is lower than the first degree of photosensitivity-imparting group substitution and higher than the second degree of photosensitivity-imparting group substitution, or (2) a reactive diluent having at least one photosensitivity-imparting group per molecule and having a fourth degree of photosensitivity-imparting group substitution measured in milliequivalents of photosensitivity-imparting group per gram, wherein the mixture of the first component and the second component has a fifth degree of photosensitivity-imparting group substitution measured in milliequivalents of photosensitivity-imparting group per gram which is higher than the first degree of photosensitivity-imparting group substitution and lower than the fourth degree of photosensitivity-imparting group substitution; wherein the weight average molecular weight of the mixture is from about 10,000 to about 50,000; and wherein the third or fifth degree of photosensitivity-imparting group substitution is from about 0.25 to about 2 milliequivalents of photosensitivity-imparting groups per gram of mixture.

2. A composition according to claim 1 further containing an additional component selected from the group consisting of a sensitizer, a photoinitiator, a solvent, and any mixtures thereof.

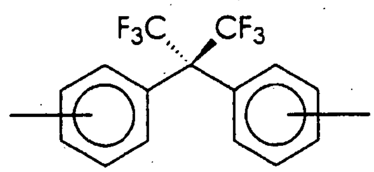
3. A composition according to either of claims 1 or 2 wherein the first component polymer has end groups derived from the "A" groups of the polymer.

4. A composition according to either of claims 1 or 2 wherein the first component polymer has end groups derived from the "B" groups of the polymer.

5. A composition according to any of claims 1 to 4 wherein A is



and B is



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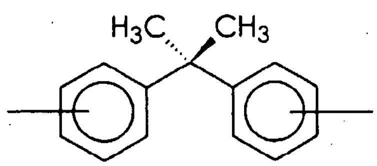

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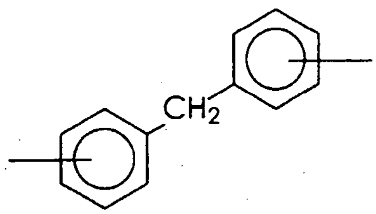

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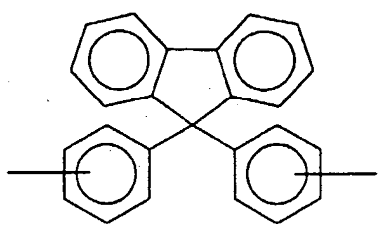

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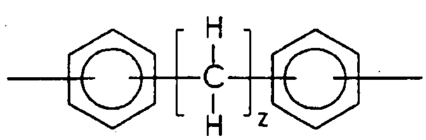
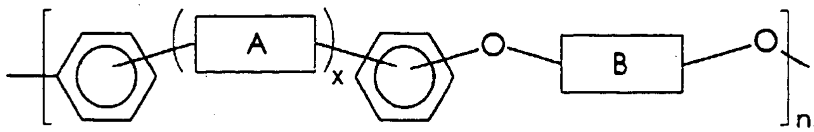


,

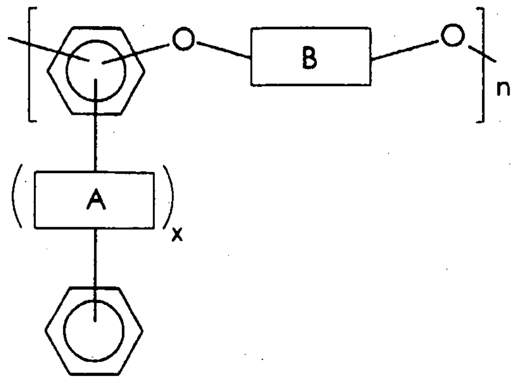
wherein z is an integer of from 2 to about 20, or a mixture thereof.

6. A process for preparing a photocurable composition having uniform weight average molecular weight and a uniform degree of unsaturated ester substitution, said process comprising the steps of:

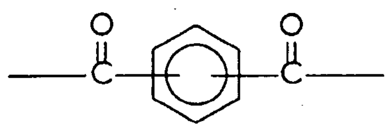
(a) providing a first component comprising a polymer, at least some of the monomer repeat units of which have at least one photosensitivity-imparting group thereon, said polymer having a first degree of photosensitivity-imparting group substitution measured in milliequivalents of photosensitivity-imparting group per gram and being of the formula



or



wherein x is an integer of 0 or 1, A is



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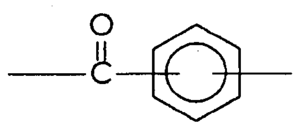

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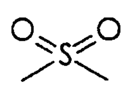

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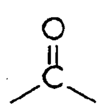

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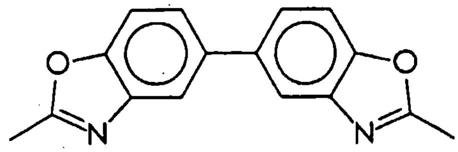
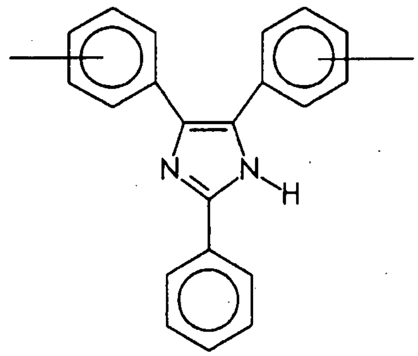
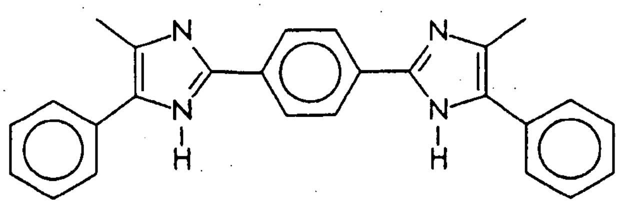


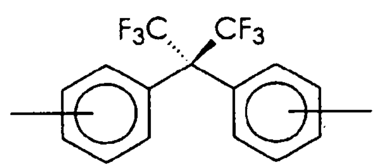


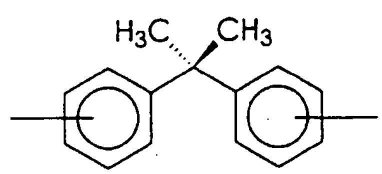


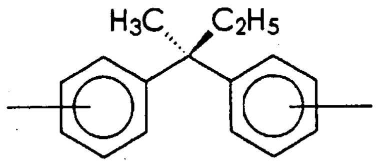
-O-,

$-C(CH_3)_2-$,

or mixtures thereof, B is






H3C
C2H5

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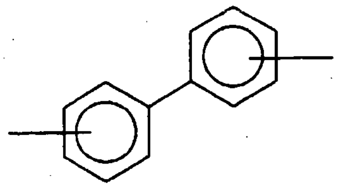

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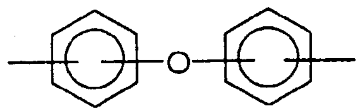
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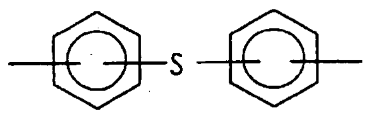
S

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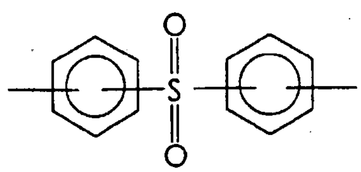
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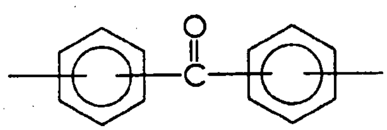
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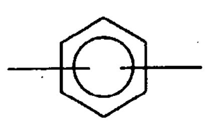

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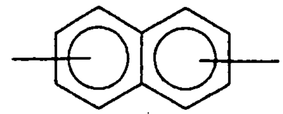
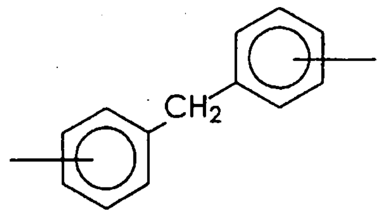
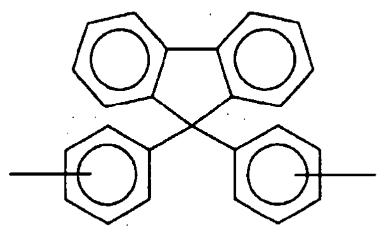
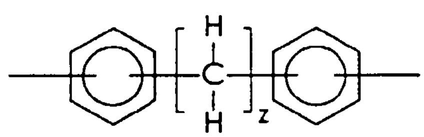
,

,

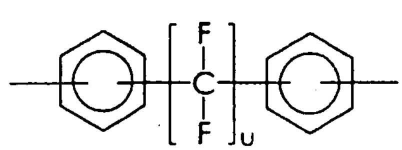
,

$$-(CH_2)_v-$$,

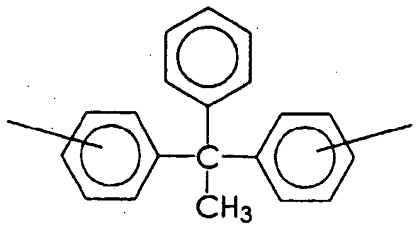
wherein v is an integer of from 1 to about 20,

,

wherein z is an integer of from 2 to about 20,

,

wherein u is an integer of from 1 to about 20,



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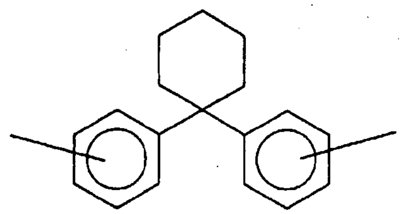

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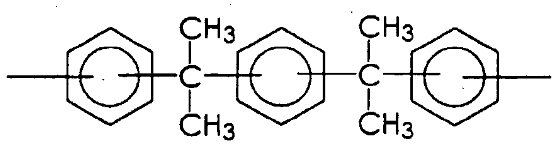

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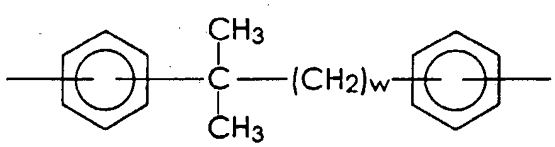

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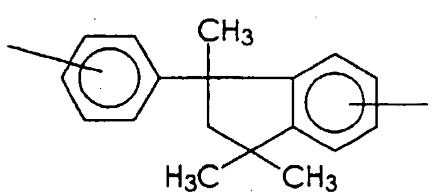
wherein w is an integer of from 1 to about 20,



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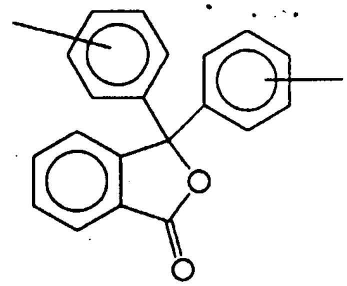

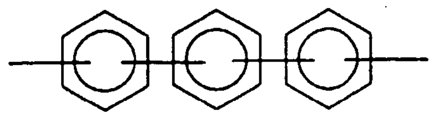

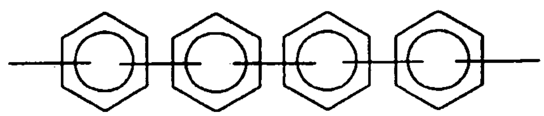

or mixtures thereof, and n is an integer representing the number of repeating monomer units;

(b) providing a second component which comprises either (1) a polymer having a second degree of photosensitivity-imparting group substitution measured in milliequivalents of photosensitivity-imparting group per gram lower than the first degree of photosensitivity-imparting group substitution, wherein said second degree of photosensitivity-imparting group substitution may be zero, or (2) a reactive diluent having at least one photosensitivity-imparting group per molecule and having a fourth degree of photosensitivity-imparting group substitution measured in milliequivalents of photosensitivity-imparting group per gram; and

(c) admixing the first component and the second component in relative amounts to result in either (1) a mixture of the first component and the polymer having a second degree of photosensitivity-imparting group substitution, said mixture having a third degree of photosensitivity-imparting group substitution which is lower than the first degree of photosensitivity-imparting group substitution and higher than the second degree of photosensitivity-imparting group substitution, or (2) a mixture of the first component and the reactive diluent having at least one photosensitivity-imparting group per molecule and having a fourth degree of photosensitivity-imparting group substitution, said mixture having a fifth degree of photosensitivity-imparting group substitution measured in milliequivalents of photosensitivity-imparting group per gram which is higher than the first degree of photosensitivity-imparting group substitution and lower than the fourth degree of photosensitivity-imparting group substitution; said mixture having a weight average molecular weight of from about 10,000 to about 50,000, wherein the third or fifth degree of photosensitivity-imparting group substitution is from about 0.25 to about 2 milliequivalents of photosensitivity-imparting groups per gram of mixture.

7. A process according to claim 6 further comprising the step of admixing with the first and second components a third component selected from the group consisting of a sensitizer, a photoinitiator, a solvent, and any mixtures thereof.

8. A process according to either of claims 7 or 8 further comprising the step of causing the first component polymer to become crosslinked or chain extended through the photosensitivity-imparting groups.

9. A process according to claim 8 wherein crosslinking or chain extension is effected either by heating the polymer to a temperature sufficient to enable the photosensitivity-imparting groups to form crosslinks or chain extensions in the polymer, or by exposing the polymer to actinic radiation such that the polymer in exposed areas becomes

crosslinked or chain extended.

10. A process for making an ink jet printhead comprising the steps of:

(a) depositing a layer (18) comprising a polymer-containing composition according to any of claims 1 to 5 onto a lower substrate (28) in which one surface thereof has an array of heating elements (34) and addressing electrodes (33) having terminal ends (32) formed thereon, said polymer being deposited onto the surface having the heating elements (34) and addressing electrodes (33) thereon;
(b) exposing the layer (18) to actinic radiation in an imagewise pattern such that the polymer in exposed areas becomes crosslinked or chain extended and the polymer in unexposed areas does not become crosslinked or chain extended, wherein the unexposed areas correspond to areas of the lower substrate (28) having thereon the heating elements (34) and the terminal ends (32) of the addressing electrodes (33);
(c) removing the polymer from the unexposed areas, thereby forming recesses in the layer (18), said recesses exposing the heating elements (34) and the terminal ends (32) of the addressing electrodes (33);
(d) providing an upper substrate (31) with a set of parallel grooves (20) for subsequent use as ink channels and a recess (24) for subsequent use as a manifold, the grooves (20) being open at one end for serving as droplet emitting nozzles; and
(e) aligning, mating, and bonding the upper (31) and lower (28) substrates together to form a printhead (10) with the grooves (20) in the upper substrate (31) being aligned with the heating elements (34) in the lower substrate (31) to form droplet emitting nozzles, thereby forming an ink jet printhead.

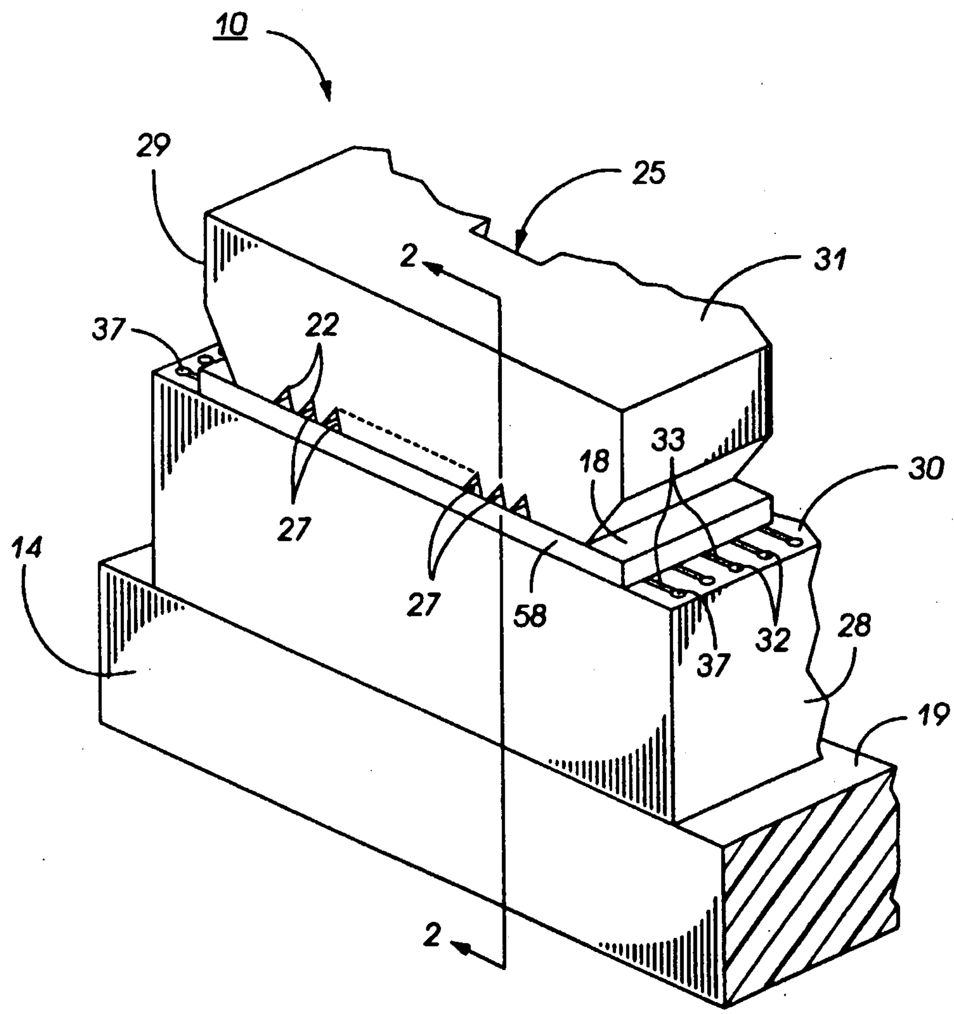

FIG. 1

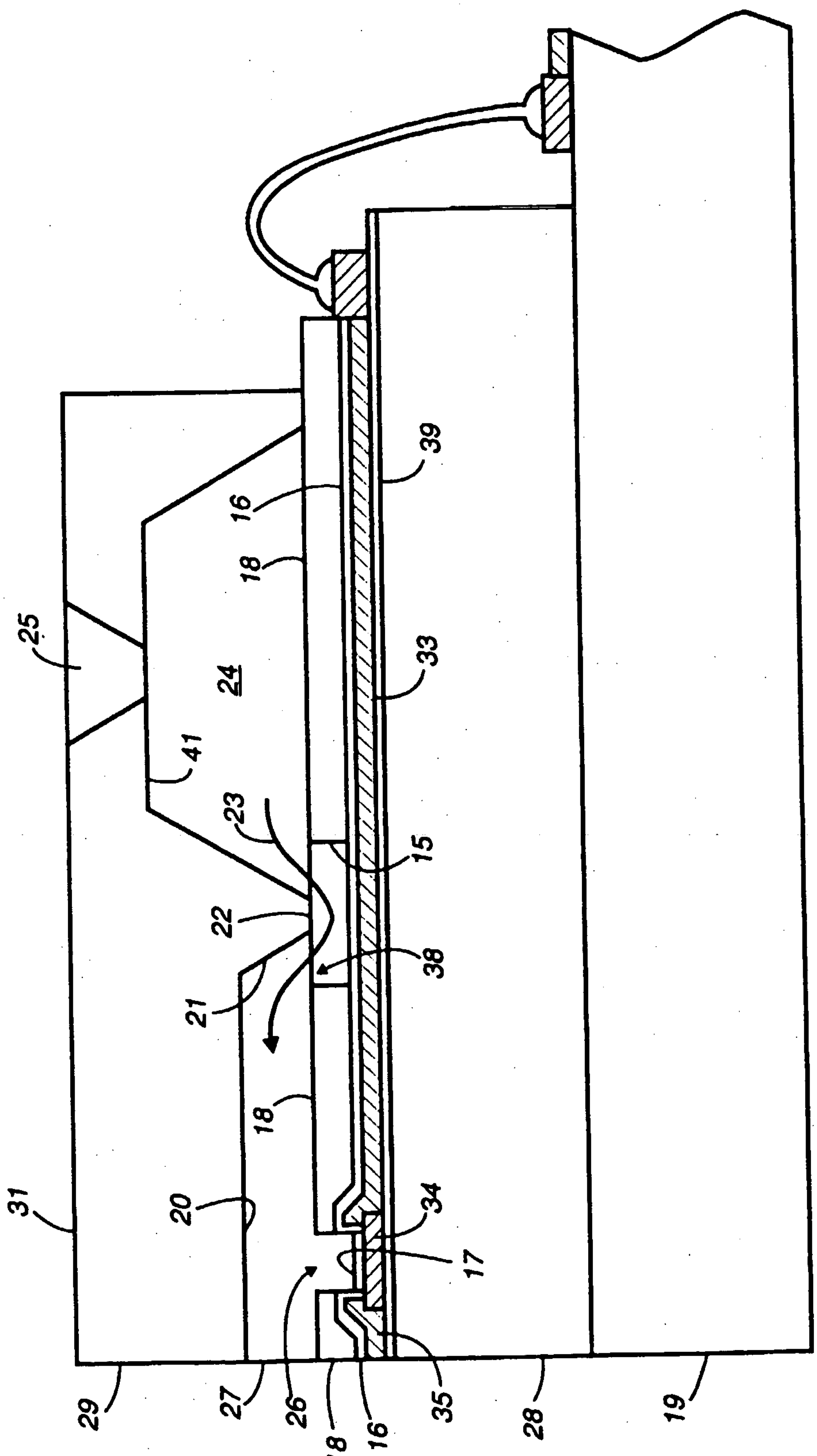
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FIG. 2

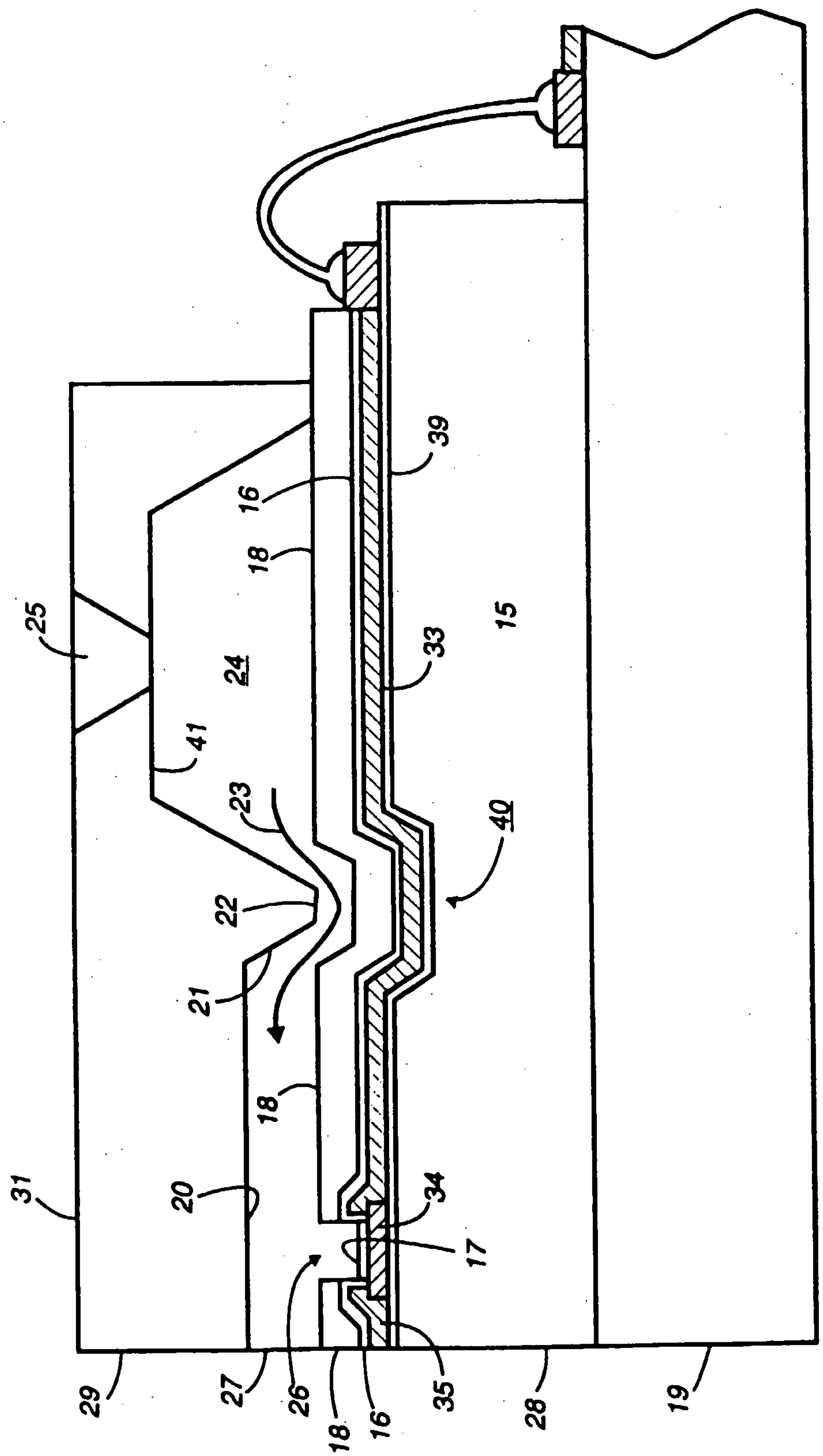
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FIG. 3